



AP/2879 EFW

Customer No. 24113

Patterson, Thuente, Skaar & Christensen, P.A.
4800 IDS Center
80 South 8th Street
Minneapolis, Minnesota 55402-2100
Telephone: (612) 349-5740
Facsimile: (612) 349-9266

Attorney Docket No. 2950.08US01

APPEAL BRIEF TRANSMITTAL

In re the application of:

	Kambe et al.	Confirmation No.: 8780
Application No.:	08/962,362	Examiner: K. Guharay
Filed:	October 31, 1997	Group Art Unit: 2879
For:	PHOSPHORS	

Mail Stop Appeal Brief-Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Transmitted herewith, in triplicate, is the Appeal Brief in the above-identified application, with respect to the Notice of Appeal filed on July 21, 2004.

Applicant(s) is/are entitled to small entity status in accordance with 37 CFR 1.27.

The Commissioner is authorized to charge to Deposit Account No. 16-0631 the \$165.00 (small entity) to cover the filing fee and any underpayments, overpayments or additionally required fees.

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01-FG-2402 165.00 DA

Respectfully submitted,


Brian L. Jarrells
Registration No. 53,067

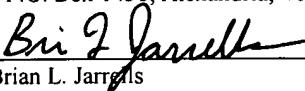
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September 21, 2004

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Brian L. Jarrells



PATENT APPLICATION

THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 2950.08US01

Kambe et al.

Confirmation No.: 8780

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For: PHOSPHORS

APPEAL BRIEF

Mail Stop Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This is an appeal from the Final Office Action dated April 22, 2004, in which claims 1-6, 20-30 and 32-34 were finally rejected. A Notice of Appeal was filed on July 21, 2004.

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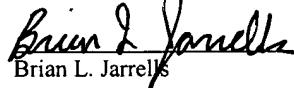
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Brian L. Jarrells

REAL PARTY IN INTEREST

NanoGram Corporation, a corporation organized under the laws of the state of Delaware, and having offices at 2911 Zanker Road, San Jose, California, has acquired the entire right, title and interest in and to the invention, the application, and any and all patents to be obtained therefore, as per the Assignment, recorded at Reel 9091, Frame 0039 from the inventors to NeoPhotonics Corporation and an assignment from NeoPhotonics Corporation to NanoGram Corporation, recorded at Reel 013957, Frame 0076. Note that NeoPhotonics Corporation was formerly called NanoGram Corporation, and the present NanoGram Corporation was previously a wholly owned subsidiary of NeoPhotonics Corporation following the formal name change. The present NanoGram Corporation is now an independent corporation, but affiliated with the earlier NanoGram Corporation, now named NeoPhotonics Corporation.

RELATED APPEALS AND INTERFERENCES

Applicants appealed the present application previously in Appeal No. 2001-2242. An RCE was filed following the rendering of the Board Decision, and the present appeal follows from a later final rejection.

STATUS OF THE CLAIMS

Claims 1-6, 20-30 and 32-34 are pending and stand rejected. Claims 7-19 and 31 have been canceled. The pending claims are listed in Appendix A.

STATUS OF AMENDMENTS

All amendments have been entered.

SUMMARY OF THE INVENTION

Applicants' invention involves display devices incorporating highly uniform fluorescent particles. The fluorescent particles emit light in response to stimulation, such as electrical stimulation. Therefore, the

particles are suitable for the incorporation into display devices wherein the particles are selectively excited to produce an image. A variety of suitable display devices and corresponding structures are described in Applicants' specification at page 22, line 4 to page 24, line 24.

The use of highly uniform particles provides for greater control over the emissions of the particles. See page 19, line 21 to page 20, line 4. Specifically, particles with a narrow particle size distribution have a corresponding light emission band covering a narrow frequency range. See page 4, lines 25-29 and page 19, line 30 to page 20, line 4. In addition, the uniformity of the particles leads to processing advantages with respect to the formation of thin layers with sharp edges. See page 20, lines 5-13. The production of highly uniform nanoparticles is enabled by the laser pyrolysis approach described in Applicants' specification.

Laser pyrolysis for particle generation involves a reactant stream that flows through an intense light beam, such as a laser beam. See, for example, page 5, lines 16-26. The light beam drives the chemical reaction. See, for example, page 7, line 24 to page 8, line 5. Because of the intense temperatures generated by absorption of light by compounds flowing through the light beam, the light beam forms a well defined reaction zone. See page 8, lines 14-15. The particles are quenched rapidly after leaving the reaction zone. See, for example, page 11, lines 16-18. Having a well defined reaction zone results in the extreme uniformity of the resulting particles. See, for example, page 11, lines 18-20.

The resulting particles produced by laser pyrolysis have a very narrow particle size distribution. In particular, the particles have a narrow distribution about the average particle size, as determined by transmission electron microscopy. See, for example, page 19, lines 4-16. Transmission electron micrographs of titanium oxide formed by laser pyrolysis from a co-pending patent application are enclosed in Appendix C, as visual confirmation of particle uniformity.

These highly uniform particles are particularly well suited for the formation of improved display devices. See, for example, page 4, lines 29-32. Sharp edges can be formed between elements of the display. See, for example, page 20, lines 8-13. The small particles are also suitable for low velocity electronic excitation with high luminosity. See, for example, page 21, lines 29-32.

ISSUES

1. Whether claims 1-6, 20-30 and 32-34 are obvious over U.S. Patent 5,442,254 to Jaskie in view of U.S. Patent 5,455,489 to Bhargava?

GROUPING OF CLAIMS

Claims 1-6 and 20-30 are within claim Group I.

Claim 32-34 are within claim Group II.

ARGUMENT

The Examiner rejected claims 1-6, 20-30 and 32-34 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent 5,442,254 to Jaskie (the Jaskie patent) in view of U.S. Patent 5,455,489 to Bhargava (the Bhargava patent). Copies of the Jaskie patent and the Bhargava patent are found in Appendix B. As noted by the Examiner, the Jaskie patent discloses a display device including fluorescent particles and the desirability of having highly uniform fluorescent particles. The Jaskie patent also discloses the concept of tuning fluorescent emissions by selecting particle size.

The Examiner noted that the Jaskie patent does not specifically describe the particle size distributions claimed by Applicants. It was the Examiner's position that the production of particles having the claimed particle size distribution was obvious. The Examiner further indicated that the Jaskie patent taught that the specification of a desired particle range was within the skill in the art. The Examiner also noted that the Jaskie patent does not disclose phosphor particles comprising a metal oxide. However, the Examiner asserted that the Bhargava patent "teaches that metal oxide particles such as ZnO (group II-VI, semiconductor) ZnS, and Y₂O₃ are all suitable for quantum contained phosphors, such as desired by Jaskie." Office Action dated April 22, 2004 at pages 2-3. The Examiner then concluded that "it would have been obvious to select ZnO, ZnS, and Y₂O₃, phosphors as disclosed by Bhargava, in the display, as disclosed by Jaskie, because selection of known materials for a known purpose is within the skill of the art." Id. at 3.

In summary, with respect to claims of Group I, Applicants argued, in response to the Examiner's assertions, that the production of particles with the claimed narrow particle distribution was not within the level of skill in the art. Furthermore, Applicants presented evidence that the discussion in the Jaskie patent does not permit the formation of narrow particle size distributions disclosed and claimed by Applicants. Specifically, as objective evidence Applicants submitted evidence that the micelle and inverse micelle approaches were not effective to form metal oxide particles. Further objective evidence had been presented with respect to the wet filtration approach of the Jaskie patent. Thus, Applicants believe that this evidence has rebutted the Examiner's assertions of obviousness.

As objective evidence with respect to the wet filtration approach, Applicants submitted a Declaration by Professor Singh, an expert in nanoparticle technology, with a preliminary Amendment dated March 24, 2000. A copy of Professor Singh's Declaration is found in Appendix C. Professor Singh's Declaration supports the Applicants position that the wet filtration approach of the Jaskie patent does not enable the production of Applicants' claimed invention. Additionally, the Applicants presented a Declaration by Professor Bricker, who is an expert in separation technologies. A copy of Professor Bricker's Declaration is found in Appendix D. The Declaration of Dr. Bricker presents an explicit and clear explanation of why the wet filtration process described in the Jaskie patent cannot and will not work for the intended purpose. The Examiner did not find the Declarations of Dr. Singh and Dr. Bricker convincing, which appears to be at least partly motivated by a previous decision rendered by the Board of Patent Appeals and Interferences on March 18, 2003.

With respect to the claims of Group II, Applicants argued that both the Jaskie patent and the Bhargava patent teach away from the from the claimed particle collections. More specifically, Applicants argued that both the Jaskie patent and the Bhargava patent disclose particles that have a diameter of 10 nm or less, and therefore teach away from phosphors particles with an average diameter of 15 nm to 100 nm.

A. Legal Background

1. Burden of Persuasion

The Applicants note that the patent office has the burden of persuasion in showing that the Applicants are not entitled to a patent. "[T]he conclusion of obviousness yet non is based on the

preponderance of evidence and argument in the record." In re Oetiker, 24 USPQ2d 1443, 1445 (Fed. Cir. 1992). The patent office has the ultimate burden of persuasion in establishing that an applicant is not entitled to a patent. Id. at 1447, concurring opinion of Judge Plager. "**The only determinative issue is whether the record as a whole supports the legal conclusion that the invention would have been obvious.**" Id.

"In rejecting claims under 35 U.S.C. §103, the examiner bears the initial burden of presenting a prima facie case of obviousness." In re Rijckaert, 28 USPQ2d 1955, 1956 (Fed. Cir. 1993). Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. In re Ochiai, 37 USPQ 1127, 1131 (Fed. Cir. 1995). ("The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'"). "**It is impermissible, however, to simply engage in a hindsight reconstruction of the claimed invention, using applicant's structure as a template and selecting elements from references to fill the gaps.**" In re Gorman, 18 USPQ2d 1885, 1888 (Fed. Cir. 1991)(emphasis added).

2. The References Must Disclose All of the Elements

Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. In re Ochiai, 37 USPQ 1127, 1131 (Fed. Cir. 1995). ("The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said subject matter pertains.'"). See also, MPEP 2143.03 "All Claim Limitations Must Be Taught or Suggested," citing In re Royka, 180 USPQ 580 (CCPA 1974). "To establish prima facie obviousness of a claimed invention, all of the claim limitations must be taught or suggested by the prior art." MPEP 2143.03.

3. The Cited References Must Provide a Reasonable Expectation of Success

Additionally, the proposition is well established that the cited art only renders a composition of matter or apparatus unpatentable to the extent that the cited art enables the disputed claims, in other words, if the cited art provides a means of obtaining the claimed composition or apparatus.

To the extent that anyone may draw an inference from the Von Brumer case that the mere printed conception or the mere printed contemplation which constitutes the designation of a 'compound' is sufficient to show that such a compound is old, regardless of whether the compound is involved in a 35 U.S.C. 102 or 35 U.S.C.

103 rejection, we totally disagree. ... We think, rather, that the true test of any prior art relied upon to show or suggest that a chemical compound is old, is whether the prior art is such as to place the disclosed 'compound' in the possession of the public.

In re Brown, 141 USPQ 245, 248-49 (CCPA 1964) (emphasis in original) (citations omitted). Similarly, see In re Hoeksema, 158 USPQ 596, 600 (CCPA 1968)(emphasis in original):

We are certain, however, that the invention as a whole is the claimed compound and a way to produce it, wherefore appellant's argument has substance. There has been no showing by the Patent Office in this record that the claimed compound can exist because there is no showing of a known or obvious way to manufacture it; hence, it seems to us that the 'invention as a whole,' which section 103 demands that we consider, is not obvious from the prior art of record.

While there are valid reasons based on public policy as to why this defect in the prior art precludes a finding of obviousness under section 103, In re Brown, *supra*, its immediate significance in the present inquiry is that it poses yet another difference between the claimed invention and the prior art which must be considered in the context of section 103. So considered, we think the differences between appellant's invention as a whole and the prior art are such that the claimed invention would not be obvious within the contemplation of 35 U.S.C. 103.

The Federal Circuit has further emphasized these issues. "But to be prior art under section 102(b), a reference must be enabling. That is, it must put the claimed invention in the hands of one skilled in the art."

In re Sun, 31 USPQ2d 1451, 1453 (Fed. Cir. 1993)(unpublished). Assertions in a prior art reference do not support an anticipation or obviousness rejection unless the references place the claimed invention in the hands of the public. Beckman Instruments Inc. v. LKB Produkter AB, 13 USPQ2d 1301, 1304 (Fed. Cir. 1989). "In order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method." Id. While a properly citable reference is prior art for all that it teaches, references along with the knowledge of a person of ordinary skill in the art must be enabling to place the invention in the hands of the public. In re Paulsen, 31 USPQ2d 1671, 1675 (Fed. Cir. 1994). See also In re Donohue, 226 USPQ 619, 621 (Fed. Cir. 1985).

4. Declaration Rebuttal Evidence

The use of declaration evidence to establish non-enablement of a patent has been addressed in the case law. "To successfully rebut the examiner's *prima facie* case of enablement, it was incumbent upon [the applicant] to introduce **affidavits** or other factual evidence in support his position." In re Payne, 203 USPQ

245, 256 (CCPA 1979) (emphasis added). “Facts, such as test data demonstration inoperativeness...or facts set forth in an **affidavit (37 CFR 1.132) of an expert in the field suggesting that inoperativeness, would be highly probative.**” Id. (emphasis added). Applicants can rebut a presumption of operability of a reference by showing by a preponderance of the evidence that the reference is inoperable. In re Sasse, 207 USPQ 107, 111 (CCPA 1980) (“He had to rebut the presumption of operability of Guillot [patents] by a preponderance of the evidence.”). Declaration evidence is sufficient to rebut the presumption of operability and operates to place the burden back onto the PTO to rebut the contention of non-enablement. Id. at 111-112. Additionally, the CCPA has stated that “we regard the opinions of experts in the field as entitled to consideration.” In re Sebek, 175 USPQ 93, 95 (CCPA 1972). With respect to the weight of expert opinions, the CCPA has stated that:

The board stated that the Henne affidavit is essentially an opinion and as such carries little weight. It seems to us that one as well qualified in the highly technical art of fluoride-containing halogenated compounds as Henne is shown to be **is properly entitled to express his expert opinions, and that such opinion is entitled to be given consideration** with the other evidence in the case in determining whether the conclusion of obviousness is supported by opinion of the examiner as to what the prior art teaches.

In re Fay, 146 USPQ 47, 51 (CCPA 1965) (emphasis added). Furthermore, MPEP § 716.01(c) indicates that “[opinion] testimony is entitled to consideration and some weight so long as the opinion is not on the ultimate legal conclusion.” “In assessing the probative value of an expert opinion, the examiner **must** consider the nature of the matter sought to be established, the strength of any opposing evidence, the interest of the expert in the outcome of the case, and the presence and absence of factual support for the expert’s opinion.” Id. (Emphasis added). Thus, it is well settled that expert opinions expressed in declarations are entitled to consideration, and that declaration evidence is sufficient to rebut the presumption of operability of a reference.

Moreover, “it is well established that enablement requires that the specification teach those skilled in the art to make and use the invention without undue experimentation.” In re Wands, 8 USPQ2d 1400, 1404 (Fed. Cir. 1988). “Whether undue experimentation is needed is not a single, simple factual determination, but rather is a conclusion reached by weighing many factual considerations.” Id. Factors to be considered in

determining whether a disclosure requires undue experimentation include "(1) the quantity of experimentation necessary, (2) the amount of direction or guidance presented, (3) the presence or absence of working examples, (4) the nature of the invention, (5) the state of the prior art, (6) the relative skill of those in the art, (7) the predictability or unpredictability of the art, and (8) the breadth of the claims." *Id.*

5. There Must Be Motivation In The Art To Modify The Teachings Of the Cited References

The motivation, or suggestion, to modify the teachings of a reference must be either explicitly or implicitly in the references or knowledge "generally available to one of ordinary skill in the art." See, MPEP § 2143.01. Furthermore, "[t]he test for an implicit showing [of motivation] is what the combined teachings, knowledge of one of ordinary skill in the art, and nature of the problem to be solved as a whole would have suggested to those of ordinary skill in the art." See, MPEP §2143.01 (quoting *In re Kotzab*, 55 USPQ2d 1313, 1317 (Fed. Cir. 2000)).

Referring to MPEP 2143.01, it is well established that "**Fact that References Can Be Combined Or Modified Is Not Sufficient To Establish *Prima Facie* Obviousness.**" Furthermore, referring to MPEP 2143 "The teaching or suggestion to make the claimed combination and the reasonable expectation of success must be both found in the prior art, and not based on applicant's disclosure." Citing *In re Vaeck*.

The Federal Circuit has provided considerable guidance on establishing obviousness of a claim. "Our case law makes clear that the best defense against hindsight-based obviousness analysis is the rigorous application of the requirement of a teaching or motivation to combine the prior art references." *Ecocolchem Inc. v. Southern Edison*, 56 USPQ2d 1065, 1073 (Fed. Cir. 2000). "Therefore, '[w]hen determining the patentability of a claimed invention which combines two known elements, 'the question is whether there is something in the prior art as a whole to suggest the desirability, and thus the obviousness, of making the combination!'" *Id.* (quoting *In re Beattie*, 24 USPQ2d 1040, 1042 (Fed. Cir. 1992)(quoting *Lindemann Maschinenfabrik GmbH v. American Hoist and Derrick Co.*, 221 USPQ 481, 488 (Fed. Cir. 1984))). "The test is not whether one device can be an appropriate substitute for another." *Ruiz v. A.B. Chance Co.*, 57 USPQ2d 1161, 1167 (Fed. Cir. 2000) (emphasis added). In *Ruiz*, the Federal Circuit

overturned a district court holding that "it would have been obvious to combine screw anchors and metal brackets, because the need for a bracket 'was apparent.'" *Id.*

The importance of the principle that the prior art itself must suggest the motivation to modify the teachings of a reference was eloquently stated in *In re Rouffet*, 47 USPQ2d 1453, 1458 (Fed. Cir. 1998)(emphasis added):

The Board did not, however, explain what specific understanding or technical principle within the knowledge of one of ordinary skill in the art would have suggested the combination. **Instead the board merely invoked the high level of skill in the field of the art. If such a rote invocation could suffice to supply a motivation to combine, the more sophisticated scientific fields would rarely, if ever, experience a patentable technical advance.** Instead, in complex scientific fields, the Board could routinely identify the prior art elements in an application, invoke the lofty level of skill, and rest its case for rejection. **To counter this potential weakness in the obviousness construct, the suggestion to combine requirement stands as a critical safeguard against hindsight analysis and rote application of the legal test for obviousness.**

"There is no suggestion to combine [references] if a reference teaches away from its combination with another source." *Tec Air Inc. v. Denso Manufacturing Michigan Inc.*, 52 USPQ2d 1294, 1298 (Fed. Cir. 1999). **"A 'reference will teach away if it suggests that a line of development flowing from the reference's disclosure is unlikely to be productive of the result sought by the applicant."** *Winner International Royalty Corp. v. Wang*, 53 USPQ2d 1580, 1587 (Fed. Cir. 2000)(quoting *In re Gurley*, 31 USPQ2d 1130, 1131 (Fed. Cir. 1994)) (emphasis added). "A reference may be said to teach away when a person of ordinary skill, upon reading the reference, would be discouraged from following the path set out in the reference, or would be led in a direction divergent from the path that was taken by the applicant." *In re Gurley*, 31 USPQ2d 1130, 1131 (Fed. Cir. 1994).

B. Declaration by Professor Singh

Applicants filed a Declaration under 37 C.F.R. §1.132 by Professor Singh with a Preliminary Amendment on March 24, 2000. A copy of Professor Singh's Declaration is presented in Appendix C. In response to Dr. Singh's Declaration submitted by Applicants, the Examiner has indicated that the Declaration had "little probative value." See the Office Action of April 25, 2000 at page 5. The Examiner further

indicated that objective evidence "should be supported by actual proof." The Examiner cited for support MPEP 716.01(c). Applicants respectfully assert that the Examiner incorrectly cited the MPEP and the underlying case law. The law is summarized above. In addition, the factors described by the MPEP for evaluating the weight of a Declaration are summarized above. In the Board of Patent Appeals and Interferences decision of March 18, 2003, the Board gave no weight to the Declaration of Professor Singh. As discussed below, the Board made clear legal errors when they gave no weight to Professor Singh's Declaration.

In view of establishing the weight to be accorded to Professor Singh's Declaration, Applicants note that Professor Singh has no interest to be gained in the present case. Dr. Singh is an expert who has consulted with many important companies in the field of nanotechnology. As noted in the Declaration, Dr. Singh has no equity interest in NanoGram. Any expert will require payment for their time. He is not an inventor and has not consulted for NanoGram in the area of phosphors, except for the Declaration under discussion. Dr. Singh has **no interest** in the outcome of the present patent application.

The Examiner indicated that Dr. Singh's Declaration was self-contradictory because of statements relating to reasons why chromatographic techniques have not been explored for the separation of inorganic nanoparticles. Applicants firmly believe that Dr. Singh's Declaration is not self-contradictory. Dr. Singh was addressing a speculative proposition, the separation of nanoparticles by size using chromatography, i.e., wet filtration in the terminology of the Jaskie patent. To state that the procedure would be difficult or impossible to scale up is one explanation of why no work has been reported on the approach or related approaches to date. Since no work had been done previously, an undue amount of experimentation would be required to attempt to practice the technique. Dr. Singh's statements directly relate to the unreasonable amount of experimentation needed to implement the process. This argumentation is **completely self-consistent**.

Applicants do not deny that generally chromatography is a well developed field for **chemical and biochemical separation**. However, this experience does not extend to the separation of solid inorganic particles. The Examiner cited isotope separation of lithium in 1938, as described in Instruments of Science, An Historical Encyclopedia (Garland Publishing, Inc.). As described in the reference on page

108, the lithium isotope separation was performed by ion-exchange chromatography. Ion exchange chromatography is performed to separate molecular ions or atomic ions in solution. Thus, $^6\text{Li}^+$ and $^7\text{Li}^+$ have slightly different equilibrium constant with respect to adsorption on the ion-exchange resin. These solvated ions have no direct relationship to inorganic nanoparticles, and they are separated by **mass not by size**. The lithium isotopes differ only by the number of neutrons that varies the mass and have an identical atomic size. The ions are dissolved in the solvent and not dispersed. The physical and chemical characteristics between the lithium ion case and inorganic particles are completely unrelated.

Since ion exchange is used for **solvated molecular or atomic ions**, there is no expectation that ion-exchange chromatography would be expected to work for dispersed inorganic nanoparticles to separate them by size. Professor Bricker's Declaration, discussed below, directly addressed the application of chromatography to the size separation of nanoparticles with respect to describing why these methods would not be expected to work. Therefore, Applicants do not believe that there is any evidence whatsoever contrary to their position and the expert opinion of Professor Singh that, minimally, an undue amount of experimentation would be required to attempt to separate nanoparticles by size using wet filtration described in the Jaskie patent or for that matter any type of chromatographic technique. The evidence of record strongly suggests that such a chromatographic separation of nanoparticles based on size would be actually impossible based on the present state of technology.

In the present case, the nature of the matter sought to be established, i.e., size separation of nanoparticles by chromatography, is at best speculative. It is difficult to establish that a method that has never been tried is not a useful approach. To establish a new method of purifying nanoparticles based on the minimal guidance from the Jaskie patent is at most an invitation to perform extensive research in the hopes that it may work. But the real issue is that an undue amount of experimentation at best would be required. Professor Singh's Declaration addressed the relevant issues from the perspective of an **expert** in the field of inorganic particles regarding the suggestions in the Jaskie patent.

Nevertheless, to confirm that Dr. Singh's expert statements were well founded, Applicants have obtained a Declaration from an expert in chromatography, Dr. Bricker, who has directly addressed the

disclosure in the Jaskie patent. Professor Bricker concluded that the Jaskie "wet filtration" will not work to separate nanoparticles. Dr. Bricker's expert Declaration has presented objective evidence to directly address the issues raised in the Jaskie patent. The conclusions that follow from Dr. Bricker's analysis are consistent with and support Dr. Singh's statements. Dr. Bricker was not aware of Dr. Singh's Declaration.

In summary, there is no evidence, which can withstand scrutiny, contrary to Dr. Singh's statements regarding the disclosure in the Jaskie patent. The Jaskie patent does not present any experimental results. Over nine years after the Jaskie patent issued, there is no public knowledge of successful application of the Jaskie approach. This failure regarding the practice of the Jaskie invention is further objective evidence against the Jaskie suggestion. Applicants have further supported the opinions in Dr. Singh's Declaration by a Declaration by Dr. Bricker, an expert in separation technologies.

C. Declaration by Professor Bricker

A Declaration by Professor Bricker under 37 C.F.R. § 1.132 is enclosed with this Appeal Brief in Appendix D. Applicants originally submitted this Declaration with an Amendment after final of October 10, 2000. The Examiner considered the Declaration untimely and did not consider the Declaration. The Applicants also submitted Professor Bricker's Declaration with an Appeal Brief filed on October 25, 2000 with the Board of Patent Appeals and Interferences. The Board of Patent Appeals and Interferences rendered a decision on March 18, 2003. A copy of the Board's decision is found in Appendix E. As discussed below, the Board committed errors of fact and law by giving no weight to Professor Bricker's Declaration.

The Jaskie patent includes a description of a "wet filtering technique" at column 7, lines 28-40. This wet filtration involves the formation of a suspension of the particles and the use of a cloth put into the suspension to draw up the particles. Professor Bricker's Declaration is specifically directed to extreme deficiencies of the wet filtration approach described in the Jaskie patent. Professor Bricker's Declaration also describes why other chromatographic techniques, including well established methods, would not be expected to accomplish the extremely fine separation needed to obtain the claimed invention.

Professor Bricker is an expert in separation technologies similar to the "wet filtration" approaches described in the Jaskie patent at column 7, lines 28-40. These separation techniques were developed for the

separation of chemical species. In addition, these techniques have been generalized for the separation of biological macromolecules, which have a nanometer size scale. Dr. Bricker's Declaration presents an explicit and clear explanation of why the process described in the Jaskie patent cannot and will not work for the intended purpose. Thus, Applicants have presented clear objective evidence that the Jaskie patent does not enable the production of Applicants' claimed invention. Applicants note that Professor Bricker has no interest in the outcome of the present application.

Together, the Declarations by Professor Singh and Professor Bricker provide overwhelming objective evidence from an expert with considerable experience in the separation of biological nanoparticles as well as the perspective of an expert in inorganic nanoparticle technology that the approach discussed in the Jaskie patent will not work produce the compositions disclosed and claimed by Applicants. Certainly, Appellants have presented clear evidence that an undue amount of experimentation would definitely be required to try to perform the wet filtration technique outlined in the Jaskie patent.

D. Error of Fact and Law In Not Giving Weight to Professor Bricker's Declaration

At page 20 of the Board Decision of March 18, 2003, the Board concluded that the Declaration of Professor Bricker was not entitled to weight. The Board reached this conclusion based on an assertion that Professor Bricker's Declaration was "based on a fundamental assumption that a process where a mixture of different sized particles is continuously loaded onto the cloth will not work to separate different size classes of quantum particles because particles are continuously remixed with particles of other sizes as additional particles are loaded onto the cloth." Decision at page 18. While this is the process explicitly described in the Jaskie patent at column 7, lines 30-31 ("The quantum contained particles (of all sizes) are suspended in a wet mixture."), the Bricker Declaration does not rely on this assumption, although the Declaration commented on this feature since the Jaskie procedure explicitly calls for this approach. More fundamental problems with the Jaskie process are also described in the Bricker Declaration. For example, "Significantly, the technique will not work because no cloth is known with the necessary properties to differentially interact with different sized particles." Bricker Declaration

at paragraph 9. Other problems with the Jaskie approach unrelated to the approach for getting the particles on the cloth are discussed in detail in paragraphs 10 and 11 as well as the end of paragraph 9 of the Bricker Declaration.

Thus, the assumption cited by the Board only related to one shortcoming of the Jaskie process pointed out by Professor Bricker. The more fundamental shortcomings relate to the lack of a known material to provide the appropriate size separation process. Thus, the Board's statements on page 18, that the particles could be loaded a single time on the cloth, do not result in a workable process without overcoming the other fatal shortcomings noted in the Bricker Declaration. The Board's statements that the particles will climb different amounts on the cloth dependent on their size reflects a misunderstanding of the process and ignores the extensive statements in paragraph 10 of the Bricker Declaration **that have nothing whatsoever to do with how the particles are loaded onto the cloth.**

The Board made a clear error of fact in ignoring major portions of the Bricker Declaration. Applicants have clearly demonstrated by a preponderance of the evidence that the Jaskie patent does not allow **a person of ordinary skill** in the art to practice a wet separation process for inorganic nanoparticles **without undue experimentation.**

Additionally, since declaration evidence is sufficient to rebut the presumption of operability and place the burden back onto the PTO to rebut the contention of non-enablement, and the Examiner has not produced any objective evidence to rebut the Bricker Declaration, the Board committed errors of law by giving no weight to Bricker Declaration, and by not finding that the Declaration of Professor Bricker established by a preponderance of the evidence of record that the wet filtration concept in the Jaskie patent is inoperable.

E. Error of Law In Not Giving Weight to Professor Singh's Declaration

At page 17, the Board concluded that the Declaration of Professor Singh was not entitled to weight. The Board reached its conclusion in part by noting that "the burden of showing lack of enablement is on appellants. Prof. Singh's conclusion that it would require an undue amount of experimentation to make the wet filtration approach work is evidently based solely on his lack of personal knowledge of any description of

the process in the literature.” Decision at page 15. Additionally, the board stated that, “since we have no evidence of a search we can give little weight to Prof. Singh’s statement that the process is not described in the literature or the conclusion that undue experimentation would be required.” *Id.* The case law discussed above clearly states that the opinions of an **expert** in the field are entitled to consideration. Furthermore, Dr. Singh, being an **expert** in the field of inorganic nanoparticles, does not need to perform a literature search as a prerequisite to opining about the state of technology in the nanoparticle art. Dr. Singh’s status as an expert in the field provides a sufficient basis for giving his opinion weight. The purpose of soliciting an expert is that they spend a majority of their time pondering issues on the state of the art by reading, reviewing and editing articles and attending and presenting at conferences to hear the state of the art. A brief review of Professor Singh’s resume will indicate to anyone that Professor Singh has an intimate familiarity with the relevant literature. The fact that he opined in a sworn Declaration is clear statement of his comfort relating to his familiarity with the relevant state of the art. Therefore, the Board’s refusal to give significant weight to Professor Singh’s Declaration constitutes an error of law.

Moreover, the case law discussed above also clearly states that an affidavit of an expert in the field suggesting the inoperativeness of a reference is highly probative, and places the burden back onto the PTO to rebut the contention of non-enablement. This legal precedent is clearly based on the expertise that an expert brings to the review process when consideration is given that the relevant enablement standards are based only on a person of ordinary skill in the art. In other words, once an applicant has come forward with objective evidence, such as declaration evidence, the burden shifts to the examiner to rebut the objective evidence of non-enablement provided by the applicant. Thus, since the Examiner has failed to provide any objective evidence to rebut the conclusions stated in Professor Singh’s Declaration, the Board committed an error of law by not finding that the Declaration of Professor Singh demonstrated by a preponderance of the evidence of record that the wet filtration concept in the Jaskie patent is inoperable.

F. Patentability of Group I over the Jaskie patent in view of the Bhargava patent

The Examiner rejected claims 1-6 and 20-30 (Group I) under 35 U.S.C. § 103(a) as being unpatentable over the Jaskie patent in view of the Bhargava patent. The Jaskie patent was cited for disclosing

phosphor particles with an average particle size less than about 100 nm. The Examiner asserted that the Jaskie patent teaches that a desired particle size distribution is within the skill in the art. The Bhargava patent is cited for disclosing metal oxide phosphor particles. However, the combined teachings of the cited references do not enable the practice of aspects of Applicants claimed invention.

At pages 5 and 6 of the Board Decision of March 20, 2003, the Board raised issues regarding the disclosure in the Jaskie patent of nanocrystals formed by the micelle or inverse micelle technique. As stated by the Board on page 6 of the Decision, "although not noted by the examiner or appellants, it appears that Jaskie discloses a method of producing particles having a highly uniform distribution of diameters within the claimed range (although Jaskie does not specifically mention the 95 percent figure)." In view of the Board's reliance on these statements, Applicants have examined these issues further.

Under conventional usage, nanocrystals generally refers to crystallites within polycrystalline particles. Thus, the size and size distribution of the crystallites does not directly reflect the particles size and size distribution. For example, as described at page 41, lines 11-13 of WO 98/37165 (of record in the present case), the average crystallite size is preferably at least about 40 percent of the average particle size in the embodiments described therein. In some circumstances, the average **crystallite size** is evaluated from measurements of the broadening of the x-ray diffractogram peaks, and no information may be provided on the **average particle size**.

Applicants previously realized the presence in the Jaskie patent of the language on the micelle techniques relied on by the Board. Since nanocrystal properties do not generally reflect the nature of the particles, Applicants assumed that the particle properties of the CdS nanocrystals did not reflect the particle properties, based on standard usage of the nanocrystal terminology. In view of the Board's decision, Applicants examined the Goldstein et al. publication in the Mat. Res. Soc. Symp. Proc. of 1991. It was not immediately clear from the paper how the particle size and size distribution are related to the crystallite size and distribution. The Board further included with their Decision, a publication by Steigerwald et al. which was also not clear about the relationship of the particle size with the crystallite size.

On further examination, Applicants found a reference to Murray et al. that clearly describe unaggregated nanocrystals when formed by the micelle approach. This reference was attached as part of an IDS submitted with a Request For Continued Prosecution and can be found in Appendix F. Applicants also attached another review from 2001 for reference by the Examiner, which is also attached in Appendix F. The particles in the Murray et al. reference are limited to sulfides, selenides and tellurides with an average particle size up to about 12 nm (120 angstroms). Thus, Applicants' present claims are patentably distinct from these materials. It is clear from the publications attached, that the state of the art did not provide an approach for the formation of Applicants' claimed materials by the micelle/inverse micelle approaches at the time of filing Applicants' application.

With respect to size separation, the Jaskie patent makes vague references to approaches to size separation of inorganic nanoparticles. In particular, the Jaskie patent discusses wet filtration as an approach for separating inorganic nanoparticles. Presumably, the vague reference in the Jaskie patent to wet filtration is based on a desire to adapt methods used for biological macromolecules for the separation of inorganic nanoparticles.

The description of wet filtration in the Jaskie patent is not well conceived, and in fact cannot and will not work for its intended purpose. To demonstrate that the wet filtration concept in the Jaskie patent is inoperable, Applicants have presented objective evidence in form of Declarations of Dr. Bricker, an expert in separation technology, and Dr. Singh, an expert in inorganic nanoparticle technology. These Declarations provide overwhelming evidence that the production of highly uniform nanoparticles, as claimed by Applicants, were not within the level of ordinary skill in the art. Specifically, Professor Bricker's Declaration indicates that other forms of chromatography would also not work, and Professor Singh's Declaration indicates that appropriate separation technologies were not known to a person of skill in the inorganic nanoparticle art. Thus, Applicants have clearly met their burden of showing by well, well beyond a preponderance of the evidence that the wet filtration concept in the Jaskie patent is not enabled, i.e., would require undue experimentation, which shifts the burden to the Examiner to provide objective evidence to rebut the Applicants assertion of non-enablement. The Examiner has failed to provide any objective evidence

that rebuts the conclusions stated in the Declarations of Professor Bricker and Professor Singh. Consequently, Applicants have established, by more than a preponderance of the evidence, that the Jaskie patent does not enable one of ordinary skill in the art to obtain Applicants' claimed invention. Furthermore, the Bhargava patent does not make up for the deficiencies of the Jaskie patent.

Moreover, even assuming arguendo that the wet filtration concept in the Jaskie patent is even theoretically possible for the separation of inorganic nanoparticles, one of ordinary skill in the art would be required to expend an undue amount of experimentation in order to accomplish the extremely fine size separation required in order to obtain Applicants' claimed invention. In particular, the Jaskie patent provides virtually no guidance in the materials suitable to perform these miraculous separations. The Jaskie patent specifically refers to the use of "cloth." Perhaps this reference to cloth is an inadvertent mistake to reference paper chromatography. Additionally, no reference is made to suitable solvents, nor are any working examples provided or experimental conditions described in the patent for performing the filtration. The extreme deficiencies of the Jaskie process are clearly and thoroughly described in Professor Bricker's Declaration. Thus, only a generic wet filtration concept is disclosed in the Jaskie patent that would, at a minimum, require extensive experimentation to practice. Since at least undue experimentation would be required to practice the wet filtration concept in the Jaskie patent, the wet filtration process concept is not enabled. An evaluation of factors laid out in the Wands case demonstrates that there is clearly no expectation of success, since there were no working examples, little if any real guidance and the nature of an invention that is theoretically ill conceived and unrelated to any other approach ever successfully used. This approach is far, far away from providing a reasonable expectation of success.

In contrast with the Jaskie approach of wet filtration, Applicants' particle production approach forms a narrow distribution of particle sizes during the formation of the particles. The average particle size can be adjusted by changing the reaction parameters. Thus, no separation of the particles is needed. Since neither the Jaskie patent nor the Bhargava patent, either alone or in combination, place the public in possession of Applicants' claimed invention, the combination of the Jaskie patent and the Bhargava patent does not render Applicants' claimed invention obvious.

The weight of the evidence viewed in its entirety does not support a finding of unpatentability. Specifically, the Patent Office has not met their burden of persuasion with respect to unpatentability. Applicants respectfully request the withdrawal of the rejection of claims 1-6 and 20-30 under 35 U.S.C. § 103(a) as being unpatentable over the Jaskie patent in view of the Bhargava patent.

G. Patentability of Group II over the Jaskie patent in view of the Bhargava patent

The Examiner rejected claims 32-34 (Group II) under 35 U.S.C. § 103(a) as being unpatentable over the Jaskie patent in view of the Bhargava patent. More specifically, the Examiner asserted that, "Jaskie does not explicitly exemplify that average particle diameter is about 15 nm to 100 nm, however it has been held that discovering an optimum value of a result, effective variable involves only routine skill in the art." Applicants submit that the Examiner has failed to establish a prima facie case of obviousness.

The Jaskie patent teaches that the desired particles have a diameter of 10 nm (100 angstroms, i.e., Å) or less. See, for example, column 3, lines 52-57, column 4, lines 6-7 and column 6, lines 46-54 ("with the **maximum size** being approximately 100 Å," emphasis added). Similarly, the Bhargava patent teaches particles that have a diameter of 10 nanometers, i.e., 100 angstroms, or less. See, for example, the abstract, column 1, lines 63-67 and column 4, lines 64-67. Thus, **both** the Jaskie patent and the Bhargava patent **teach away** from phosphor particles with an average diameter of 15 nm to 100 nm.

Since the cited references alone or together do not teach, suggest or motivate the claimed invention, and since the cited references teach away from the claimed particle collections, the combined disclosures of the Jaskie patent and the Bhargava patent clearly do not render claims 32-34 prima facie obvious.

Since the combined disclosures of the Jaskie patent and the Bhargava patent do not render Applicants' claimed invention prima facie obvious, Applicants respectfully request withdrawal of the rejection of claims 32-34 under 35 U.S.C. § 103(a) as being unpatentable over the Jaskie patent in view of the Bhargava patent.

CONCLUSIONS

Applicants submit that claims 1-6, 20-30 and 32-34 are unobvious over the prior art of record. Applicants believe that the Patent Office has failed to meet their burden of persuasion with respect to unpatentability of any of the claims in view of the total evidence presented. Thus, Applicants Respectfully request the reversal of the rejections of claims 1-6, 20-30 and 32-34.

Respectfully submitted,



Brian L. Jarrells
Registration No. 53,067

Customer No. 24113
Patterson, Thuente, Skaar & Christensen, P.A.
4800 IDS Center
80 South 8th Street
Minneapolis, Minnesota 55402-2100
Telephone: (612) 252-1535

APPENDIX A

1. A display device comprising phosphor particles having an average diameter less than about 95 nm and wherein the phosphor particles comprise a first collection of particles having a diameter distribution such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter and the phosphor particles comprising a metal oxide.
2. The display device of claim 1 wherein the phosphor particles comprise a metal compound selected from the group consisting of ZnO, TiO₂ and Y₂O₃.
3. The display device of claim 2 wherein the metal compound is ZnO.
4. The display device of claim 1 wherein the phosphor particles have an average diameter from about 5 nm to about 50 nm.
5. The display device of claim 1 wherein the phosphor particles have a diameter distribution such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.
6. The display device of claim 1 wherein the light emission follows low velocity electron excitation.
20. The display device of claim 1 wherein the phosphor particles further comprise a second collection of particles, the second collection of particles having a diameter distribution such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.
21. The display device of claim 1 wherein the phosphor particles are in contact with an anode.

22. The display device of claim 1 further comprising a liquid crystal layer.
23. The display device of claim 1 further comprising a partially light transparent substrate.
24. The display device of claim 1 further comprising a transparent electrode comprising indium tin oxide.
25. The display device of claim 1 further comprising an electrode to guide the electrons from the cathode to the anode.
26. The display device of claim 1 wherein the display is an electroluminescent display.
27. The display device of claim 1 wherein the device is a field emission device with the phosphor particles located between an anode and cathode.
28. The display device of claim 27 comprising a plurality of anodes and cathodes where each electrode pair forms an addressable pixel.
29. The display device of claim 1 wherein the phosphor particles are roughly spherical.
30. The display device of claim 1 wherein the phosphor particles are excitable by low velocity electrons.

32. A display device comprising a collection of phosphor particles having an average diameter from about 15 nm to about 100 nm and having a diameter distribution such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.

33. The display device of claim 31 wherein the phosphor particles comprise a metal compound selected from the group consisting of ZnO, ZnS, TiO₂ and Y₂O₃.

34. The display device of claim 1 wherein the phosphor particles are roughly spherical.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Kambe et al.

Serial No.: 08/962,362

Filed : October 31, 1997

Group Art Unit:
2879

For : PHOSPHORS

Examiner: M. Day

Docket No. : N19.12-0006

DECLARATION UNDER 37 C.F.R. § 1.132

Express Mail: EL418983858US
Date of Deposit: March 24, 2000

Assistant Commissioner for Patents
Washington, D.C. 20231

I, Rajiv K. Singh, Ph.D., hereby declare as follows:

1. I am presently a Professor of Material Science and Engineering at the University of Florida at Gainsville. Also, I am also Director of the Characterization, Research Instrumentation and Testbed Facility of the Engineering Research Center for Particle Science and Technology at the University of Florida. Apart from my academic responsibilities, I provide consulting services through R. K. Singh Consulting Inc.
2. I received my Ph.D. degree in 1989 in Material Science and Engineering from North Carolina State University, Raleigh, NC.
3. I have been on the faculty at the University of Florida since 1990. I was promoted to Associate Professor with tenure in 1995 and to full Professor in 1997. A copy of my Curriculum Vitae is attached.
4. My recent accomplishments include receiving a National Science Foundation Young Investigator Award in 1994 and the Hardy Gold Metal for Outstanding Contributions in Material Science in 1995. I was a Distinguished Visiting Professor/Scientist at National University of Singapore (1999) and National Institute for Materials and Chemical Research, Tsukuba, Japan (2000). I am the

author or co-author of more than 293 scientific articles and conference proceedings. I have co-edited five books and guest edited five journal issues.

5. I am under a Consulting Agreement with NanoGram Corporation to provide consulting services in the area of chemical-mechanical planarization. I am not a shareholder in NanoGram Corporation.

6. I have read carefully the pending claims of the above noted patent application entitled "PHOSPHORS" and U.S. Patent 5,442,254 to Jaskie (the Jaskie patent). I did not participate in any capacity with the preparation of the PHOSPHORS patent application.

7. I am very familiar with approaches that have been attempted for separating nanoparticles by filtration. To my knowledge, no experimental results based on the separation of nanoparticles by the wet filtration approaches described in the Jaskie patent at column 7, lines 28-40 have ever been reported in the public literature. Since such chromatography techniques are not known for the separation of nanoparticles, a person of skill in the art would expect to expend a substantial amount of inventive effort to attempt to practice the wet filtration techniques. Without at least some preliminary results to support the basic principles underlying the effort, there would be no reasonable expectation of eventual success at applying the wet filtration approach. In my opinion, the wet filtration approaches described in the Jaskie patent at column 7, lines 28-40 are highly speculative, and the description in the Jaskie patent does not provide a reasonable expectation of successfully separating a collection of nanoparticles to isolate a particle population with a desired narrow range of particle sizes.

8. Since the Jaskie wet filtration techniques would be difficult or impossible to scale up to commercial quantities, it is unlikely that any effort will ever be spent on developing such approaches. The only possibility for the expenditure of experimental effort on such wet filtration techniques would be to

satisfy academic curiosity. In the biological sciences, gel electrophoresis is an important technique for the characterization of biochemical preparations. However, there are other long established approaches for characterizing nanoparticles.

9. I am aware of considerable amounts of effort expended using conventional size exclusion filtration for the preparation of nanoparticle collections. At the time of filing the PHOSPHORS patent application on October 31, 1997, there were no filtration approaches publicly known that could create a collection of phosphorescent nanoparticles with a very narrow size distribution as disclosed and claimed in the PHOSPHORS patent application. At best, these filtration techniques could only exclude micron scale contaminants.

10. Based on my extensive knowledge in the nanoparticle field, it is my opinion that the "tuning (size selection)" described in the Jaskie patent at column 7, lines 28-30 could not be accomplished based on publicly available filtration methods as of October 31, 1997. Specifically, tuning could not be performed by the wet filtration approach outlined in the Jaskie patent without the expenditure of an undue amount of experimentation, if at all.

11. I declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: March 21 '00

By: Rajiv K. Singh
Rajiv K. Singh, Ph.D.

RAJIV K. SINGH
 Materials Science and Engineering
 University of Florida
 Gainesville, FL 32611-2066
 (352) 392 1032
 (352) 392 3771 (fax)
 email: rsing@mail.mse.ufl.edu

Research Interests:

Innovative processing of materials; Laser processing; thin films; transient thermal phenomena; superconducting and dielectric (low K and high K) thin films; diamond and related materials, rapid thermal processing of elemental and wide band gap semiconductors, chemical-mechanical planarization, particulate coatings; semiconductor processing; modeling of transient thermal processing; flat panel displays, Angstrom scale advanced materials characterization, oxide thin films & electronics, gallium nitride and diamond crystal growth, nanoparticle synthesis and processing, front and back end semiconductor cleaning, phosphors and flat panel displays, thin film batteries.

Education

Ph.D. Materials Science and Engineering, North Carolina State University, Raleigh, 1989
 M.S. Materials Science and Engineering, North Carolina State University, Raleigh, 1987
 B.S. Chemical Engineering, Jadavpur University, Calcutta, India, 1985

Positions Held

97-pre *Professor*, Materials Science and Engr., University of Florida
 94-pre *Director*, Characterization Research Instrumentation and Testbed (CRIT) Facility, Engineering Research Center (ERC), University of Florida
 96-pre *Thrust Leader*, Chemical Mechanical Planarization (CMP), ERC Univ of Florida
 94-pre *Thrust Leader*, Engineered Particulates, ERC, Univ. Florida
 95-97 *Associate Professor*, Materials Science and Engr., University of Florida
 90-94 *Assistant Professor*, University of Florida, Gainesville, FL

Awards/Honors

2000 - *Distinguished Visiting Scientist*, NIRIM, Tsukuba, Japan
 1999 *Distinguished Visiting Professor*, National University of Singapore, Singapore
 1998 *Distinguished Visiting Professor*, University of Osaka, Osaka, Japan
 1995 *Hardy Gold Medal* from TMS/AIME for Outstanding Contributions in Materials Science
 1994 *NSF Young Investigator Award*
 94-97 *Visiting Fellow*, Center for Ultrafast Optical Science (CUOS), University of Michigan
 1993 *IEEE Senior Member Award*
 1991 *IBM Faculty Development Award*
 1989 *MRS Best Graduate Student Award*
 1985 *Alumni Gold Medal* for Best Overall Graduating Senior from the University
 1985 *Laha Silver Medal* for Best Graduate from College of Engineering

Publications:

Over 293 papers (> 268 published/in print & 25 submitted for various materials science and engineering journals (*Science*, *Physical Review B*, *Applied Physics Letters*, *Journal of Materials Research*, *Materials Science and Engineering B*, etc.) and Conference Proceedings. Published over 32

original, *principal author papers in App. Phy. Lett.* (The most cited electronic materials/applied physics based journal), and 7 papers published in *Physical Review B*

Invited and Contributed Talks

Presented more than 110 invited talks at international conferences (MRS, SPIE, TMS, APS, ASME, etc.) and academic and research institutions (MIT, Columbia, Purdue, ORNL, Westinghouse, etc.). Also group presented over 250 technical papers at international conferences

Books and Guest Editorships (Edited 5 books & Guest Editor of 5 Journal Issues)

- (1) R. K. Singh, D. Norton, J Cheung and J. Narayan and L.D. Laude, *Eds "Laser Processing of Materials: Fundamentals and Advanced Applications*, MRS Proceedings Vol 397, Pittsburgh, PA, 1996
- (2). N. M. Ravindra and R.K. Singh, "Transient Thermal Processing of Materials", TMS, Warrendale April. 1996
- (3). K. Gonsalves, M. Baraton, J.. Chen, J. Alkara, R. K. Singh and H. Hofmann , "Surface Controlled Nanoscale and Microscale Materials for High Value Added Applications, MRS Proceedings Vol 501 , Pittsburgh, PA, March 1998
- (4). R.K. Singh, D. Lowdnes, J. Narayan, D. Chrisey , T. Kawai, and E. Fogarassy, Editors, *Advances in Laser Ablation of Materials*", MRS Proceedings for Spring 1998 .
- (5). R. K. Singh and D. Kumar, "Advances in Pulsed Laser Deposition of Thin Films", Kluwer publishers, (1998)
- (1)Guest Editor of September 1994, Vol 23 issue of *Journal of Electronic Materials* titled " Novel Issues in Photonic Materials"
- (2) Guest Editor of Jan,96, Vol 1 issue of *Journal of Electronic Materials* titled "Ion and Laser Beam Processing of Electronic Materials"
- (3) Guest Editor of Materials Science and Engr. B, on *Laser Processing of Electronic Materials*, Jan 1997
- (4) Guest Editor of November 1997 Issue of *Journal of Electronic Materials* on "Low Energy Beam Processing of materials."
- (5)Guest Editor of September 1998 Issue of *Journal of Electronic Materials* on "Chemical-Mechanical Polishing of Semiconductors.

Teaching Accomplishments

Developed four new courses:"Beam-Solid Interactions", "Thin Films" & "Math. Methods", "Survey of Materials Analysis" in the graduate MS&E program

Graduated 12 Master's and 10 Ph.D Students; Presently thesis advisor to 9 Ph. D Students
8 students awarded best paper/fellowships for their undergraduate/graduate research projects.

Developing CD-ROM materials and multi-media classroom for the NSF ERC project.

Established ParTiN (Particle technology) Hypertext Network for educational &ERC programs on the WWW (World Wide Web)

Corporate Interactions

Direct Research Interactions with several companies including IBM, Intel, Motorola, Ashland Chemical, Westinghouse, Lucent Technology, Applied Materials, Sony, Glaxo Wellcome, Lockheed Martin, Astra Zeneca, Purdue Pharma

Licensing Discussions with Sony, Nara Machinery, Astra Zeneca, Glaxo, etc.
Corporate funding over 200 K/yr .

Copyrighted Softwares (3 copyrighted softwares) including

(A) **SLIM** (*Simulation of Laser Interaction with Materials*, 36,000 coded lines, 1992) software. This first of its kind software is being used by more than 50 R&D groups (IBM, LANL, ORNL, etc.) in the world. This software calculates the transient thermal induced laser effects like melting, crystallization and ablation of materials. This software has had sales greater than \$ 60 K worldwide in the last four years. Two new versions (one based on DOS C++ and the other on Windows platform) have been developed..

Patents (from a total of 30 disclosures:[14 patents, 10 awarded/pending(final stage) and 4 filed])

- (1) **High Surface Area Metals and Ceramics** [US Patent 5,473,138] . A unique laser technique has been developed to increase the surface areas of ceramics, metals and composites. This technique involves the use of multiple-pulse laser irradiation under controlled energy window conditions.
- (2) **Enhanced Chemical Vapor Deposition of Diamond** [US Patent 5,485,804 {1996}, Filed for worldwide patent} Novel colloidal method for large area nucleation, of diamond. *This method has been used to make the world's largest single monolithic piece of diamond which has a diameter greater than 11" and weighs over 1600 carats.*

Conference Chairs [Organized 16 international conferences on innovative processing and characterization of materials]

- (1) Chair of Symposium. on "Beam Processing of Materials", *TMS/AIME Winter meeting*, Chicago Nov 92;
- (2) Co-Chairman of Symposium on "Innovative Processing of Electronic and Photonic Materials" *TMS/AIME Annual Meeting*, Denver, Feb 1993;
- (3) Chairman of Conference on "Advanced Laser Processing of Materials" *Engineering Foundation Conf.*, Palm Coast, FL, May 1-6 1994;
- (4) Chair of Symposium on " Ion Beam Processing of Materials" *TMS Spring Meeting*, LasVegas, Feb 1995
- (5) Co-Chair of symposium on "Laser Processing of Materials" *American Physical Society*, San Diego, March 1995
- (6) Chair of Symposium on " Advanced Laser Processing of Materials: Fundamentals and Advanced Applications" *MRS Meeting*, Boston Nov 1995
- (7) Co-Chair, Symposia on "Transient Thermal Processing of Materials", *TMS Annual Meeting*,Anaheim, CA Feb, 1996
- (8) Chairman of symposium on, " Low Energy Beam Processes", *TMS Annual Meeting*, Orlando , FL Feb, 1997
- (9) Chairman of symposium on " Particulate Coatings", *MRS Fall Meeting*, Boston November, 1997
- (10) Co-Chairman of " Laser and Ion Beam Processing of Materials", *International Union of Materials Research Societies (IUMRS)*, Chiba, Japan, September 1997
- (11) Co-Chairman, " Transient Thermal Processing of Materials , *TMS Annual Meeting*, San Antonio, Feb 1998
- (12) Co-Chairman, " Chemical Mechanical Planarization of Materials Symposia, *TMS Annual Meeting*, San Antonio, Feb 1998
- (13) Chairman, " Advances in Pulsed Laser Ablation of Materials", *MRS Spring Meeting*, San Francisco, April, 1998

- (14) Co-Chairman, "Particulate Coatings" 5th World Congress on Particle Science and Technology, Brighton UK, July 1998
- (15) Co-Chairman "Rapid Thermal Processing of Materials"- European MRS Meeting, Strasbourg, June, 1998
- (16) Chairman, "Chemical Mechanical Polishing Symposia", *MRS Spring Meeting*, San Francisco, April 2000

Invited Review Articles

- 1. "Pulsed Laser Deposition of Thin Films", *Materials Science and Reports* in March, (1998)
- 2. "SLIM, A Personal Computer Based Simulation of Laser Interaction With Materials", *J. Journal of Materials*, 44, 20 (1992)
- 3. "Pulsed Laser Deposition and Processing of Superconducting Thin Films", *J. of Materials* 43, 13 (1991)

Book Chapters

- 1. D. Gilbert and R. K. Singh, "Boron Nitride Interfaces", in "Properties of Group III Nitrides", Edited by James Edgar, *Imspec* publication, London 1995
- 2. R. K. Singh, "Raman Based Optical Properties of YBaCuO Surfaces", in "Optical Properties of Materials", Eds R. Hummel, CRC Press, 1996
- 3. R.K. Singh and D. Kumar, "Pulsed Laser Deposition of Superconducting Thin Films", *Materials Science and Engr. Reports* (in press, 1996)
- 4. R. K. Singh and D. Kumar, "Thermal Annealing of Semiconductors", *Encyclopedia of Applied Physics*, VCH Publishers (1996)
- 5. D. Gilbert and R. K. Singh, "Diamond Deposition for Electronic Applications", Eds . S. Pearton on *Wide Band Gap Semiconductors*", VCH Publishers 1997

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Reviews

Reviewer for NSF, DOE, Physical Review B, Materials Science and Engineering, Journal of Applied Physics, Applied Physics Letter, Journal of Materials Research and Physica C. Invited to serve as panel members for several NSF initiatives

Memberships and Committee Chairmanships:

Member of MRS, ASM, TMS, IEEE (senior member), APS, AIChE, SPIE
 Chairman: Thin Films and Interfaces Committee , TMS (1993 -1996)
 Member: Laser Processing of Materials Committee, CLEO

Institutional Impact

- (A) Helped establish the 60 million, NSF Funded *Engineering Research Center (ERC)* on particle science and technology at the University of Florida:
- (B) Leader of team for the NSF MRSEC Proposal submitted in 1995 & 1997
- (C)Established cross-disciplinary multi P.I programs in Rapid Thermal Processing, Particle Coating Technology, Radiation Damage in Electronic Devices, and Beam Processing of Materials:
- (D) Established industrial and scientific collaborations with various institutions:
- (E) Established international collaborations with

(i) CNRS, Strasbourg France, (ii) University of Melbourne, Australia, (iii) University of Osaka, Japan, (iv) Keio University, Japan, (v) EPFL, Lausanne, Switzerland, (vi) Unicamp, Sao Paulo Brazil, (vii) National University, Singapore

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Kambe et al.

Serial No.: 08/962,362

Filed : October 31, 1997

For : PHOSPHORS

Docket No.: N19.12-0006

Group Art Unit: 2879

Examiner: M. Day

DECLARATION UNDER 37 C.F.R. § 1.132

Express Mail: EL636050305US
Date of Deposit: October 10, 2000

BOX AF
Assistant Commissioner for Patents
Washington, D.C. 20231

I, Terry M. Bricker, Ph.D., hereby declare as follows:

1. I am presently the Mooreland Family Professor of Basic Sciences, Department of Biological Sciences and an adjunct Professor of Chemistry at Louisiana State University, Baton Rouge, Louisiana.
2. I received my Ph.D. degree in 1981 in Botany from Miami University.
3. I have been on the faculty at the Louisiana University since 1987. I was promoted to Associate Professor with tenure in 1990 and to full Professor in 1994. A copy of my Resume is attached.
4. I have been Visiting Professor at the University of Illinois and Michigan State University. I am the author or co-author of many scientific articles, conference proceedings and review papers. I have served on the editorial board of Plant Physiology and the Annual Reviews of Plant Physiology and Plant Molecular Biology.
5. I have no financial interest in NanoGram Corporation or in the present patent application.

6. I have extensive experience in separation technology applied to biological nanoparticles, in particular, proteins and DNA. I and coworkers in my laboratory continuously use several forms of chromatography in the separation and purification of proteins. I have used chromatography and protein purification techniques throughout my career.

7. I have read carefully U.S. Patent 5,442,254 to Jaskie (the Jaskie patent). I have evaluated the description of particle separation in the Jaskie patent based on my extensive expertise in separation technology generally.

8. The isolation method of the quantum particles describe in the Jaskie patent at column 7, lines 28-40 relies on the use of capillary action to separate particles of different diameters. Specifically, particles with a diameter range of about 10 to 100 angstroms are suspended in a liquid, and the liquid is allowed to move up a cloth by capillary action. The authors argue that the distance which various particles migrate up the cloth is directly proportional to their size. The authors further suggest that at any given height up the cloth all of the particles will be the same size. Thus, the authors are describing a chromatographic system which they allege will differentially fractionate the particles based on size.

9. The separation techniques described in the Jaskie patent will not separate different size classes of quantum particles. First, a mixture of different sized particles is continuously loaded onto the cloth. Even assuming for argument that the different sized particles migrate at different speeds, additional particles are continuously loaded behind the migrating edge of initially loaded particles. Thus, the particles are continuously remixed with particles of other sizes as additional particles are loaded onto the cloth. This remixing occurs for every size class of particles. Significantly, the technique will not work because no cloth is known with the necessary properties to differentially interact with different sized particles.

Traditional thin layer chromatography is based on differential solubility constants for the chemicals being separated. Due to different solubility constants, solutes migrate at different rates as the solvent is taken up by capillary action.

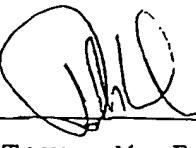
10. Any chromatographic separation approach relies on 1) the properties of the liquid that the particles are suspended in, 2) the surface characteristics of the cloth, 3) the surface properties of the quantum particles, and 4) the size of the quantum particles. The patentees provide no direct information on the first three of these categories. Based on the discussion in the previous paragraph in column 7 of the patent, perhaps one can assume that the solvent is water. However, the surface properties of the cloth used in the described separation is critical. Separation in any chromatographic system is dependent on differential partitioning of the solutes, i.e., the quantum particles, between a mobile phase, the water, and a stationary phase, the cloth. However, no such cloth exists. For separation of biological macromolecules, such separation by size is the purview of gel filtration chromatography. Even in gel filtration fractionation systems, the relatively small differential partitioning coefficients observed prevent true high resolution separations. In this particular instance, one must necessarily obtain high degrees of dimensional resolution of the quantum particles to achieve wavelength selectivity. The required dimensional resolution cannot be achieved by the methods presented in column 7, lines 28-40 of the Jaskie patent.

11. The addition of an electric field would not overcome these problems. First, the authors do not make any claim that the surface charge on the particles is directly proportional to the size. The authors do not describe the means of attaching the electric current or even if the current is applied axially or perpendicular to the capillary flow. Critically, the authors do not describe the properties of the cloth even though the properties of the cloth would critically effect the separation in

the presence of the electric field. While gel electrophoresis is used to separate biological macromolecules using electric fields, these separation are performed in polymer gels, not cloth, that have been developed for the specific purpose of separating biological macromolecules. The gel acts as a sieve, allowing the fractionation of the biological macromolecules by size, surface charge and steric properties. No cloth exists with the required sieving properties. Even the protocols effective to separate different types of biological macromolecules, such as water soluble proteins, membrane proteins and nucleic acid fragments, are significantly different from each other. Inorganic particles are very different with respect to chemical properties and chemical structure from biological macromolecules. The Jaskie patent provides no information that guides anyone trying to adapt these biochemical methods to the separation of quantum particles. Thus, a person familiar with the separation technologies could not separate Jaskie's quantum particles based on information provided in the Jaskie patent.

12. I declare that all statements made herein that are of my own knowledge are true and that all statements that are made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: 10/8/00

By: 

Terry M. Bricker, Ph.D.

RESUME

Dr. Terry M. Bricker
Position: Professor

EDUCATION:

INSTITUTION AND LOCATION	DEGREE	YEAR CONFERRED	FIELD OF STUDY
Miami University Univ. Missouri	Ph.D. Postdoctoral Work	1981 1981-1985	Botany Biological Sciences

RESEARCH AND PROFESSIONAL EXPERIENCE:

National Science Foundation, IGERT Pre-proposal Panel, 9/00.
Interim Chairperson, Department of Biological Sciences, 6/99-8/00.
Moreland Family Professor of Basic Sciences, Department of Biological Sciences, 4/99-Present
Invited Speaker, Gordon Research Conference Photosynthesis-Biochemical Aspects, 6/99.
Editorial Committee, Annual Reviews of Plant Physiology and Plant Molecular Biology - Vol. 52, 10/98.
Adjunct Professor, Department of Chemistry, Louisiana State University, 3/98-Present.
Professor, Department of Biological Sciences, Louisiana State University, 7/97-Present.
Professor and Chairman, Department of Microbiology, Louisiana State University, 7/95-6/97.
National Science Foundation, Research Training Grant site visit team to Penn State University, 6/96
National Science Foundation, Research Training Grant Advisory Panel, 4/96
Discussion Leader, Gordon Research Conference, "Photosynthesis - Biochemical Aspects", 8/96
Visiting Professor, Department of Plant Biology, University of Illinois 1/95-6/95.
Professor, Department of Plant Biology, Louisiana State University, 8/94-7/95.
Visiting Faculty, Plant Biochemistry Intensive Summer Course, MSU-DOE Plant Research Laboratory, Michigan State University, 6/94.
Associate Professor, Department of Botany, Louisiana State University, 8/90-7/94.
Invited Speaker, Gordon Research Conference, "Photosynthesis - Biochemical Aspects", 8/93.
Director, Protein Analysis Center, College of Basic Sciences, 7/90-8/92.

Dr. Terry M. Bricker
Page Two

Graduate Coordinator, Department of Botany, Louisiana State University, 9/89-8/92.

Department of Energy, *Ad hoc* Advisory Panel Basic Energy Biosciences, 1991.
National Science Foundation Molecular Biochemistry Program Advisory Panel,
10/90-4/94.

Assistant Professor, Department of Botany, Louisiana State University, 8/87-8/90.
Editorial Board, *Plant Physiology*, 1/90-7/92.

Assistant Professor, Department of Chemistry, University of Southern
Mississippi, 1/85-8/87.

Publications (last five years, only)

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55. Bricker, T.M. and Frankel, L.K. "The Role of Carboxylic Acid Residues on the Manganese-Stabilizing Protein in its Binding to Photosystem II." To appear *Biochemistry*.
54. Wu, J., Masri, N., Lee, W., Frankel, L.K. and T.M. Bricker, "Directed Random Mutagenesis in the Large Extrinsic Loop of the CP 47 Protein of Photosystem II." *Plant Molecular Biology* 39,381-386 (1999).
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48. Bricker, T.M., Putnam-Evans, C. and J. Wu, "Mutagenesis in the Study of the Structure and Function of Photosystem II." *Methods of Enzymology* 297:320-337 (1998).
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PATTERSON, THUENTE, SKAAR
& CHRISTENSEN, P.A.

Paper No. 30

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

MAILED

MAR 18 2003

PAT. & T.M. OFFICE
BOARD OF PATENT APPEALS
AND INTERFERENCES

Ex parte NOBUYUKI KAMBE
and XIANGXIN BI

Appeal No. 2001-2242
Application 08/962,362¹

ON BRIEF

Before JERRY SMITH, BARRETT, and RUGGIERO, Administrative Patent Judges.

BARRETT, Administrative Patent Judge.

DECISION ON APPEAL

This is a decision on appeal under 35 U.S.C. § 134 from the examiner's final rejection of claims 1-6 and 20-30, all the pending claims in the application.

We affirm.

¹ Application for patent filed October 31, 1997, entitled "Phosphors."

BACKGROUND

The disclosed invention involves fluorescent particles with average dimensions of 5 to 100 nanometers (nm), called nanoparticles, which have a very uniform distribution of diameters. The fluorescent particles emit light in response to electrical stimulation. Therefore, the particles are suitable for incorporation into display devices wherein the particles are selectively excited to produce an image. The use of highly uniform particles provides for greater control over the emissions of the particles. Particles with a narrow particle size distribution have a corresponding light emission band covering a narrow frequency range (color). The uniformity of the particles leads to processing advantages with respect to the formation of thin layers with sharp edges. Nanoparticles with a very narrow particle size distribution are produced by a laser pyrolysis system described in the disclosure, but not claimed. These highly uniform particles are particularly well suited for the formation of improved display devices.

The following claim further illustrates the invention.

1. A display device comprising phosphor particles having an average diameter less than about 100 nm and wherein the phosphor particles comprise a collection of particles having a diameter distribution such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

Appeal No. 2001-2242
Application 08/962,362

The examiner relies on the following references:

Jaskie	5,442,254	August 15, 1995
Bhargava	5,455,489	October 3, 1995

Claims 1, 4-6, 20-25 and 27-30 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Jaskie.

Claims 2, 3, and 26 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Jaskie in view of Bhargava.

We refer to the final rejection (Paper No. 18) (pages referred to as "FR") and the examiner's answer (Paper No. 24) (pages referred to as "EA") for a statement of the examiner's rejection, and to the appeal brief (Paper No. 23) (pages referred to as "Br") and the reply brief (Paper No. 25) (pages referred to as ("RBr") for a statement of appellants' arguments thereagainst.

OPINION

Grouping of claims

The claims are argued to stand or fall together (Br5). Therefore, for purposes of this appeal, the claims will stand or fall together with claim 1.

The disclosed and claimed invention

Appellants describe a laser pyrolysis system for "the production of particles with a highly uniform size distribution and structural homogeneity" (spec. at 11, lines 19-20). The "collection of particles has an average diameter ... preferably

from about 5 nm to about 100 nm" (spec. at 18, lines 5-8). In addition, "the particles generally have a distribution of sizes such that at least 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter" (spec. at 19, lines 6-10). The specification describes that very small particle diameters allow for adjustment of emission characteristics without the need to activate the particles with a second metal (spec. at 20, lines 1-4) and that the particles may be phosphors (spec. at 21, lines 15-16).

Appellants seek to claim phosphor particles having a particular average size (i.e., "an average diameter less than about 100 nm" in claim 1) and uniformity (i.e., "about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter" in claim 1), the average diameter $\pm 60\%$, without claiming the method of producing the particles. The size and uniformity of the particles are said to result from the disclosed laser pyrolysis system; however, since the laser pyrolysis system is not claimed, particles having the claimed size and uniformity produced by any process will satisfy the claims.

It is apparently appellants' position (although not expressly stated) that they are entitled to broadly claim the particle size and uniformity limitations without claiming the

method of production because they were the first ones to come up with a method that allows production of particles having these uniformity characteristics.

The rejection over Jaskie

Jaskie discloses that the properties of quantum contained particles are designed chiefly by selecting the size (diameter) (col. 6, lines 39-41). It is disclosed that the color of the emitted light is adjusted, or tuned, by adjusting the size distribution of the particles during manufacture (col. 6, lines 43-46). It is disclosed that 50 Å (5 nm) diameter particles have a yellow to yellow orange color, reducing the size of the particles moves the emitted color to the blue end of the spectrum, and by increasing the size, the emitted color is moved toward the red end of the spectrum, with the maximum size being 100 Å (10 nm) (col. 6, lines 46-54). The particle materials provide luminescence (col. 5, lines 6-12) and are "phosphors," as claimed. Thus, Jaskie discloses quantum contained phosphor particle sizes approximately 10 times smaller than appellants' particle sizes and used for the same purpose.

Jaskie discloses two methods of manufacturing quantum contained particles, the micelle or inverse micelle technique and an etching technique (col. 6, line 62 to col. 7, line 27), and a method of size selection (col. 7, lines 28-40). The micelle or

inverse micelle technique is described to produce nanocrystals where "[v]ariations in size are generally in the range of $\pm 7\%$ in diameter" (col. 7, lines 10-11). Accordingly, although not noted by the examiner or appellants, it appears that Jaskie discloses a method of producing particles having a highly uniform distribution of diameters within the claimed range (although Jaskie does not specifically mention a 95 percent figure).

Nevertheless, we also consider the examiner's reasoning.

The examiner finds that Jaskie does not disclose the claimed range of particle sizes (FR3). The examiner states (FR3): "Jaskie teaches, however, that the specification of a desired particle range is within the level of skill of the art. See col. 7, lines 34-40. It would have been obvious to specify a desired particle range because the specification of a desired particle range is generally recognized to be within the skill of the art." Appellants admit that "the Jaskie patent discloses ... the desirability of having highly uniform fluorescent particles" (Br5) and do not appear to challenge the examiner's conclusion.

The examiner further reasons that taking particles in Jaskie having a yellow color with a 50 Å (5 nm) size as the average particle size, the narrower $\pm 40\%$ range of particle size recited in claim 5 would require a range of particle sizes from 3 to 7 nm (FR3). The examiner reasons that the wavelength range of visible light from 400 to 800 nm would yield a particle distribution of

from 4.14 to 5.84 nm which is within this range (FR3). That is, yellow light has a wavelength of about 590 nm which corresponds to a 5 nm particle size. Assuming the particle size is proportional to the wavelength, then blue light (at one end of the visible light range) with a wavelength of 400 nm has a particle size of 3.39 nm and red light (at the other end of the visible light range) with a wavelength of 700 nm (note that Jaskie discloses a range of 400 nm to 690 nm for visible light, col. 1, line 49) has a particle size of 5.93 nm, which is within the claimed range of particle sizes. Appellants do not challenge this reasoning. We agree that one of ordinary of ordinary skill in the art would have been motivated from Jaskie to select a highly uniform distribution of particles sizes in order to maintain a desired color. If one skilled in the art wanted to maintain a yellow color, for example, the range of particle sizes would be narrower than for the range of visible colors in the examiner's example.

The issue

Appellants do not contest that Jaskie discloses or makes obvious the particle size and uniformity limitations of claim 1. And, appellants do not contest that Jaskie discloses how to make particles having the claimed sizes mixed with other sizes. Instead, appellants argue that Jaskie does not enable one skilled

in the art to separate out particles into a batch having the claimed distribution range of sizes. Therefore, it is apparently appellants' position (although not expressly stated) that they are entitled to broadly claim the particle size and uniformity limitations without reciting the method of production because they were the first ones to come up with a method that allows production of particles having the claimed distribution of sizes.

The issue is whether Jaskie contains an enabling disclosure for making particles having the claimed distribution range of sizes. We agree that the disclosure must be adequate to permit one of ordinary skill in the art to make particles of the claimed size and size distribution. See Motorola Inc. v. Interdigital Technology Corp., 121 F.3d 1461, 1471, 43 USPQ2d 1481, 1489 (Fed. Cir. 1997) ("In order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method.").

Jaskie is presumed enabled

Jaskie claims "particles each quantum confined by a diameter dictated by a specific desired color of emitted light" (claim 1) and having a diameter "less than approximately 100 Å" (claim 9). Jaskie discloses that a specific desired color, say yellow, corresponds to a particle diameter of about 50 Å (5 nm). For the particles to have a diameter dictated by the specific color

yellow, the diameters must be within a fairly narrow range around this diameter, much narrower than the range claimed by appellants, or other colors will be produced. Thus, the claims require particles of the claimed size and size distribution. Since Jaskie is a patent, it must be presumed that the disclosure enables one skilled in the art to make these particles. The presumption of validity puts the burden on appellants to prove that Jaskie does not have an enabling disclosure, rather than on the Office to prove that it does. The presumption may be overcome by sufficient evidence.

Jaskie teaches a method of preparing particles with uniform size

Jaskie discloses (col. 6, line 62 to col. 7, line 1):

There are presently a wide variety of methods for manufacturing quantum contained particles, at least one of which uses a Micelle technique that basically allows the particles to be made in a bucket using wet chemistry. The Micelle technique is a method of precipitation in a fluid in the presence of a stabilizer that binds to the growing crystal, preventing further growth or agglomeration.

Jaskie describes an inverse micelle² example for making "nanocrystals (col. 7, lines 1-9) and states that "[v]ariations in size are generally in the range of $\pm 7\%$ in diameter" (col. 7, lines 10-11), implying that most particles are within this range, which is well within the claimed range. Thus, this technique of

² A description of "micelle" from the McGraw-Hill Encyclopedia of Science & Technology, Vol. 11 (7th ed. McGrawHill, Inc. 1992), pp. 117-118, is attached.

making nanoparticles does not appear to require size selection. Jaskie refers to a symposium paper, "Observations of Melting in 30 Å Diameter CdS Nanocrystals" by A.N. Goldstein, V.L. Colvin, and A.P. Alivasatos, in "Clusters and Cluster Assembled Materials," Materials Research Society Symposium Proceedings, Fall 1990, at col. 7, lines 11-17, which we consider to be incorporated by reference. A copy of this paper is attached. The paper states (p. 271-72): "New developments in chemical methods of preparation, have enabled the synthesis of narrow size distributions of highly crystalline, nanometer size, crystallites of inorganic semiconductors like CdS and GaAs" (emphasis added). One footnote to this sentence refers to an article entitled "Surface Derivatization and Isolation of Semiconductor Cluster Molecules," by M.L. Steigerwald et al., J. Am. Chem. Soc. 110, 1988, pp. 3046-3050 (copy attached), which describes preparing molecules of semiconductor solid that are size-selected, in particular, clusters that "have a mean cross sectional dimension of 17(3) by 19(5) Å (where the numbers in parentheses are one standard deviation)" (p. 3048). Since one standard deviation includes about 68% of the things being measured and two standard deviations includes about 95% of the things being measured, it can be seen that two standard deviations is 17 ± 6 by 19 ± 10 Å which is within the claimed distribution. Although the Goldstein and Steigerwald references are not applied in the rejection, they are

indirectly relied on by Jaskie and clearly demonstrate that it was known to those in the art how to prepare nanoparticles with uniform size distributions.³ We find that Jaskie describes making nanocrystals by an inverse micelle technique with a $\pm 7\%$ range of variation of diameter. Appellants do not address this disclosed method of making nanocrystals of a uniform size either in the arguments or the expert declarations.

Jaskie also describes manufacturing quantum contained structures down to 10 Å by common etching techniques (col. 7, lines 17-27). It appears that these structures could be considered particles; claim 1 does not require the particles to be in a free or powder form.⁴ However, this method does not describe a range of particle sizes. Appellants do not address this method of making quantum contained structures.

³ This technique of isolating clusters of nanoparticles [nanoclusters] of specific sizes by terminating the particle surfaces is also evidenced by the discussion of nanoclusters in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 18 (4th ed. John Wiley & Sons 1996), pp. 842-843, 859 (copy attached) at p. 843: "With the proper surface-capping agents, clusters of varying sizes can be isolated as powders" Kirk-Othmer is a standard reference work that is cited only to substantiate facts in the evidentiary showing.

⁴ This manufacturing technique also appears to be mentioned in Kirk-Othmer, p. 843: "[S]emiconductor nanoclusters can be directly synthesized in the polymer film (26-30).".

Appellants' arguments and expert declarations are not persuasive to show that Jaskie lacks an enabling disclosure

Jaskie discloses (col. 7, lines 28-40):

The tuning (size selection) is also accomplished in a variety of ways, at least one of which includes a wet filtering technique. The quantum contained particles (of all sizes) are suspended in a wet mixture. One end of a cloth is immersed in the liquid and the mixture is allowed to move up the cloth by capillary action, aided by an electric field if desired. The quantum contained particles will move up the cloth a distance directly proportional to their size. Thus, at a predetermined height on the cloth all of the quantum contained particles will be substantially the same size. Utilizing this or a similar technique the quantum contained particles can be easily separated into desired sizes.

This describes a method of separating quantum contained particles based on their size.

Appellants argue that "the production of particles with the claimed narrow particle size distribution was not within the level of skill in the art" (Br6) and "the discussion in the Jaskie patent [of wet filtration at col. 7, lines 28-40] did not permit the formation of the narrow particle size distributions disclosed and claimed by Applicants" (Br6) as evidenced by the declarations of Professor Singh and Professor Bricker (Br6). That is, it is argued that the wet filtration method of Jaskie does not enable one of ordinary skill in the art to make the claimed invention. Appellants' arguments are best addressed in connection with the declarations on which they are based.

Singh declaration

Professor Singh is a consultant to the assignee NanoGram Corporation (Singh decl. ¶ 5) and therefore is not a totally disinterested party. Nevertheless, Prof. Singh has impressive credentials and his testimony must be given weight.

Initially, we note that Prof. Singh's declaration does not address making of uniform sized particles by the disclosed inverse micelle technique in Jaskie, which is said to produce particles having a variation in size of $\pm 7\%$ (col. 6, line 62 to col. 7, line 17). Nor has Prof. Singh discussed Jaskie's description of making quantum confined structures by etching (at col. 7, lines 17-27), where the particles are on a surface instead of in a free form. Prof. Singh's education and experience do not appear to be in the area of preparing nanoparticles by the chemical inverse micelle technique or the etching technique. Thus, even if Prof. Singh's declaration is persuasive as to nonenablement of Jaskie's wet filtration process, the declaration fails to show that other methods in Jaskie do not enable one of ordinary skill to make the claimed invention. Although the declaration is not persuasive for this reason, we nevertheless also consider Prof. Singh's testimony regarding the wet filtration method.

Prof. Singh states that, to his knowledge, no experimental results based on the separation of nanoparticles by the wet

filtration process described by Jaskie have ever been reported in the literature (Singh decl. ¶ 7) and since such chromatography techniques are not known for the separation of nanoparticles, a person of ordinary skill in the art would be expected to expend a substantial amount of inventive effort to practice the wet filtration technique and, absent at least some preliminary results, there would be no reasonable expectation of success (Singh decl. ¶ 7). Prof. Singh offers his opinion that the wet filtration approaches in Jaskie are highly speculative (Singh decl. ¶ 7). Prof. Singh states that based on his extensive knowledge in the nanoparticle field, it is his opinion that tuning could not be performed by the wet filtration approach outlined in Jaskie without the expenditure of an undue amount of experimentation (Singh decl. ¶ 10).

The examiner states that Prof. Singh "fails to disclose what data basis [sic, databases], public records, or patent files" (EA6) were searched, or "what search terms, logical statements, or search strategy" (EA6) were applied to support his statement that wet filtration is not described in the literature (EA6).

Appellants responds that "Professor Singh is one of the best experts in the world to attest to such a fact, i.e., that the Jaskie separation approach is not known to persons of skill in the art" (RBr5-6) and "Professor Singh is an invited speaker at most of the major particle science conferences in the world and

is, thus, aware of the cutting edge research being performed in the world" (RBr6).

While Prof. Singh's has impressive credentials, a person cannot be expected to know everything in the art. This is the reason for the hypothetical person of ordinary skill standard in obviousness. We think it is not unreasonable, in questioning the enablement of a patent, to require some searching of the literature rather than reliance on personal knowledge to support a statement that Jaskie's method was not described in the literature. The burden of showing lack of enablement is on appellants. Prof. Singh's conclusion that it would require an undue amount of experimentation to make the wet filtration approach work is evidently based solely on his lack of personal knowledge of any description of the process in the literature. However, since we have no evidence of a search we can give little weight to Prof. Singh's statement that the process is not described in the literature or the conclusion that undue experimentation would be required. Prof. Singh's statement that the filtration approach in Jaskie is highly speculative is a mere conclusion which is not supported by any factual reasoning as to why the process would be unlikely to work as described. Thus, these statements by Prof. Singh are not entitled to weight.

The examiner states that the declaration does not present any experimental results, evidence of tests conducted, methods

evaluated, or any factual evidence, but consists of mere arguments and conclusions (EA5-6).

Appellants argue that no experiments are performed without relying on the experience of the experimenters, experiments must be designed and interpreted, and "Professor Singh's Declaration is ... based on a multitude of experiments performed by himself and his students [over the years]" (RBr4).

Nevertheless, past experiments which form the basis for Prof. Singh's experience and expertise are not experiments which show whether the wet filtration in Jaskie will work. In any case, the declaration does not provide any factual reasons, based on such prior experiments, why the wet filtration method in Jaskie would not be expected to work.

Prof. Singh states that since the Jaskie wet filtration technique would be difficult or impossible to scale up to commercial quantities, it is unlikely that any effort will ever be spent on developing such approaches (Singh decl. ¶ 8).

Whether or not effort would be spent developing the Jaskie process does not tend to show that the Jaskie technique is unworkable as described to one of ordinary skill in the art.

Prof. Singh states that at the time of filing there were no filtration approaches publicly known that could create a collection of phosphorescent nanoparticles with a very narrow

size distribution and, at best, these filtration techniques could only exclude micron scale contaminants (Singh decl. ¶ 9).

This statement can be considered to be related to the statement in Jaskie that "[t]he tuning (size selection) is also accomplished in a variety of ways" (col. 7, lines 28-29) and the question of whether one of ordinary skill in the art knew of other ways to perform size selection. Assuming it is correct that there were not other publicly known filtration approaches for nanoparticles, this does not prove that the wet filtration approach will not work and does not prove that other approaches for size selection were not known.

For the reasons stated above, the declaration of Prof. Singh is not entitled to weight.

Bricker declaration

The declaration by Professor Bricker, submitted with the amendment after final on October 10, 2000 (Paper No. 21), was deemed untimely by the examiner and it was noted that it would not be considered in the advisory action of October 20, 2000 (Paper No. 22). Nevertheless, since the examiner's answer refers to the declaration by Prof. Bricker, it appears to have been considered and will be addressed here.

Initially, we note that Prof. Bricker's declaration also does not address making of uniform sized particles by the

disclosed inverse micelle technique in Jaskie, which is said to produce particles having a variation in size of $\pm 7\%$ (col. 6, line 62 to col. 7, line 17). Nor does Prof. Bricker discuss Jaskie's description of making quantum confined structures by etching (at col. 7, lines 17-27). Prof. Bricker's education and experience do not appear to be in the area of preparing nanoparticles by the chemical inverse micelle technique or the etching technique. Thus, even if Prof. Bricker's declaration was persuasive as to nonenablement of Jaskie's wet filtration process, the declaration fails to show that other methods in Jaskie do not enable one of ordinary skill to make the claimed invention. Although the declaration is not persuasive for this reason, we nevertheless also consider Prof. Bricker's testimony regarding the wet filtration method.

Prof. Bricker's declaration of unworkability seems to be based on the fundamental assumption that a process where a mixture of different sized particles is continuously loaded onto the cloth will not work to separate different size classes of quantum particles because particles are continuously remixed with particles of other sizes as additional particles are loaded onto the cloth (Bricker decl. ¶ 9). We interpret this to mean that if it is assumed that 50 Å particles climb to 10 inches and 30 Å particles climb to 11 inches, under Jaskie's technique one can never separate out 50 Å particles because there is always some

smaller particles on their way through this zone on the way to a higher point in a continuous process.

The flaw in this reasoning is that Jaskie does not say that the process must be continuous (or commercial). The process can be a one-time run where the particles climb to a level depending on their size and the cloth is cut at an appropriate zone to retrieve particles of a specific desired size range. Because the declaration seems to be based on an erroneous assumption, Prof. Bricker's declaration is not persuasive.

Prof. Bricker also discusses that Jaskie provides no direct information on the properties of the liquid that the particles are suspended in, the surface characteristics of the cloth, or the surface properties of the quantum particles (Bricker decl. ¶ 10). It is stated that "the surface properties of the cloth used in the described separation is critical" (Bricker decl. ¶ 10) and that no cloth exists which provides differential partitioning of the solutes, i.e., the quantum particles, between a mobile phase and a stationary phase, the cloth (Bricker decl. ¶ 10). It is argued that the addition of an electric field would not solve these problems (Bricker decl. ¶ 11).

To the extent these reasons are dependent on the assumption of a continuous process, the reasons are not persuasive as already discussed. In addition, we note that the description in Jaskie is directed to the person of ordinary skill in the art,

which is the art of separating solid inorganic nanoparticles, and thus does not need to disclose details which would be known to the person of ordinary skill. Prof. Bricker's declaration is not persuasive because it relies on the lack of express teachings of materials in Jaskie without addressing what would have been known one of ordinary skill in the art.

Jaskie also discloses that "[t]he tuning (size selection) is also accomplished in a variety of ways" (col. 7, lines 28-29), although the only way described is wet filtering. Assuming that Prof. Bricker is correct that Jaskie does not enable one skilled in the art to make the claimed narrow particle size distributions by the wet filtration process, there is no evidence that one skilled in the art would not know of any other way to provide the required size selection.

For the reasons stated above, the declaration of Prof. Bricker is not entitled to weight.

Millipore product literature

Appellants cite product information in the brief from Millipore Corporation (Millipore) to show that commercial filters are not an effective means of creating narrow particle size distributions (Br15).

The examiner states that the fact that appellants have found a vendor that provides a filter that is not suitable for

nanoparticle separation is not persuasive evidence that no such filter exists (EA7).

Appellants respond that the Millipore represents the latest advances in filtration technology for improving size uniformity and the fact that it is dated two years after appellants' filing date and does not disclose the filters has significant probative value (RBr6).

We agree with the examiner's position. The purpose of Millipore filters is to retain the small number of defect causing "large" particles (> 1 micron) without retaining the desirable, small particles (30 to 200 nm). This does not prove that filters to filter out particles outside of a certain range do not exist or cannot be built. Appellants' argument based on Millipore is not persuasive that Jaskie is not enabled.

Parker patent

In the examiner's answer, the examiner refers to U.S. patent 5,460,701 to Parker et al. as disclosing the use of a mechanical filter for the collection of nanocrystals (EA7). Parker is not applied in any ground of rejection.

Appellants argue that while Parker describes a filter for collecting nanoparticles, the collection process does not discriminate in size and is not relevant to the issue of size

separation to produce a more uniform collection of particles (RBr7).

We agree with appellants' argument and find the examiner's reasoning to be unpersuasive.

Lithium separation

In the final rejection, the examiner referred to the use of chromatography to separate lithium-6 from lithium-7 (FR6).

Appellants argue that while chromatography is a well developed field for chemical and biochemical separation, this experience does not extend to the separation of solid inorganic particles by size (Br11). It is argued that the examiner's reference to isotope separation of lithium is nonpersuasive because there is no expectation that ion-exchange chromatography would be expected to work for inorganic nanoparticles to separate them by size (Br11-12).

The examiner does not rely on the lithium example in the examiner's answer. Nevertheless, we agree with appellants' argument and find the examiner's reasoning to be unpersuasive.

Conclusion

We find that Jaskie discloses a method of making nanoparticles having a variation in size of $\pm 7\%$. This teaching has not been addressed in appellants' arguments or in the

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declarations of Prof. Singh or Prof. Bricker and, so, it has not been demonstrated that Jaskie does not enable one of ordinary skill in the art to make the claimed invention. In addition, we are not persuaded by the declarations of Prof. Singh and Prof. Bricker that Jaskie does not enable one skilled in the art to make the claimed invention for the reasons discussed in connection with those declarations. Accordingly, we conclude that appellants have not shown error in the rejection of claim 1. The rejections of claims 1-6 and 20-30 are sustained.

No time period for taking any subsequent action in connection with this appeal may be extended under 37 CFR § 1.136(a).

AFFIRMED

Jerry Smith

JERRY SMITH
Administrative Patent Judge

Lee E. Barrett

LEE E. BARRETT
Administrative Patent Judge

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Appeal No. 2001-2242
Application 08/962,362

PETER S. DARDI
PATTERSON, THUENTE, SKAAR & CHRISTENSON, P. A.
4800 IDS CENTER
80 SOUTH 8TH STREET
MINNEAPOLIS, MN 55402-2100

Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites

C. B. Murray, D. J. Norris, and M. G. Bawendi*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 22, 1993

Abstract: A simple route to the production of high-quality CdE (E = S, Se, Te) semiconductor nanocrystallites is presented. Crystallites from ~ 12 Å to ~ 115 Å in diameter with consistent crystal structure, surface derivatization, and a high degree of monodispersity are prepared in a single reaction. The synthesis is based on the pyrolysis of organometallic reagents by injection into a hot coordinating solvent. This provides temporally discrete nucleation and permits controlled growth of macroscopic quantities of nanocrystallites. Size selective precipitation of crystallites from portions of the growth solution isolates samples with narrow size distributions ($<5\%$ rms in diameter). High sample quality results in sharp absorption features and strong "band-edge" emission which is tunable with particle size and choice of material. Transmission electron microscopy and X-ray powder diffraction in combination with computer simulations indicate the presence of bulk structural properties in crystallites as small as 20 Å in diameter.

I. Introduction

The study of nanometer sized crystallites provides an opportunity to observe the evolution of material properties with size. This intermediate size regime is where the collective behavior of bulk materials emerges from the discrete nature of molecular properties. The differing rates with which each of the bulk properties develops provides the possibility of observing and perhaps controlling novel behavior. Nonlinear optical effects from highly polarizable excited states and novel photochemical behavior are two such examples.¹

The physical properties of semiconductor nanocrystallites are dominated by the spatial confinement of excitations (electronic and vibrational). Quantum confinement, the widening HOMO-LUMO gap with decreasing crystallite size, and its implications for the electronic structure and photophysics of the crystallites have generated considerable interest.^{1,2} A number of optical studies have begun probing the photoexcited states in such crystallites.^{1,2}

Although considerable progress has been made in the controlled synthesis of II-VI semiconductor crystallites,^{1,3} interpretation of sophisticated optical experiments often remains difficult due to

polydispersities in size and shape, surface electronic defects due to uneven surface derivatization, and poor crystallinity. The study of an appropriate high quality model system is essential in distinguishing properties truly inherent to the nanometer size regime from those associated with variations in sample quality. Each sample must display a high degree of monodispersity (size, shape, etc.), regularity in crystallite core structure, and a consistent surface derivatization (cap).

This paper presents a relatively simple synthetic route to the production of high-quality nearly monodisperse ($<5\%$ rms in diameter) samples of CdE (E = S, Se, Te) nanometer size crystallites, with the emphasis on CdSe. The synthesis begins with the rapid injection of organometallic reagents into a hot coordinating solvent to produce a temporally discrete homogeneous nucleation. Slow growth and annealing in the coordinating solvent results in uniform surface derivatization and regularity in core structure. Size selective precipitation provides powders of nearly monodisperse nanocrystallites which can be dispersed in a variety of solvents. The crystallites are slightly prolate with an aspect ratio of 1.1 to 1.3. The average crystallite size, defined by its major axis, is tunable from ~ 12 to ~ 115 Å. Room temperature optical absorption and luminescence experiments show that the samples are of high optical quality. Transmission electron microscopy and X-ray powder diffraction are used in combination with computer simulations to characterize nanocrystallite structural features.

II. Experimental Section

General. All manipulations involving alkylcadmium, silylchalcogenides, phosphines, and phosphine chalcogenides were carried out using standard airless procedures. Tri-*n*-octylphosphine [TOP] and bis(trimethylsilyl) sulfide [(TMS)₂S] were used as purchased from Fluka. Electronic grade (99.99+%) selenium and tellurium shot were purchased from Alfa. Anhydrous methanol, 1-butanol, pyridine, and hexane were purchased from a variety of sources. Tri-*n*-octylphosphine oxide [TOPO] was purchased from Alfa and purified by distillation, retaining the fraction transferred between 260 and 300 °C at ~ 1 Torr. Dimethylcadmium [Me₂Cd] was purchased from Organometallics Inc. and purified by filtration (0.250 µm) and vacuum transfer. Bis(trimethylsilyl)selenium [(TMS)₂Se] and Bis(*tert*-butyl(dimethylsilyl))tellurium [(BDMS)₂Te] were prepared via literature methods^{3,4} and stored at -35 °C in a drybox. Appropriate masses of selenium and tellurium shot were dissolved directly

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Synthesis of CdE Semiconductor Nanocrystallites

in sufficient TOP to produce 1.0 M stock solutions of trioctylphosphine selenide [TOPSe] and trioctylphosphine telluride [TOPTe].⁵

Method 1. The typical preparation of TOP/TOPO capped CdSe nanocrystallites follows: Fifty grams of TOPO is dried and degassed in the reaction vessel by heating to ~200 °C at ~1 Torr for ~20 min, flushing periodically with argon. The temperature of the reaction flask is then stabilized at ~300 °C under ~1 atm of argon.

Solution A is prepared by adding 1.00 mL (13.35 mmol) of Me₂Cd to 25.0 mL of TOP in the drybox. Solution B is prepared by adding 10.0 mL of the 1.0 M TOPSe stock solution (10.00 mmol) to 15.0 mL of TOP. Solutions A and B are combined and loaded into a 50-mL syringe in the drybox.

The heat is removed from the reaction vessel. The syringe containing the reagent mixture is quickly removed from the drybox and its contents delivered to the vigorously stirring reaction flask in a single injection through a rubber septum. The rapid introduction of the reagent mixture produces a deep yellow/orange solution with an absorption feature at 440–460 nm. This is also accompanied by a sudden decrease in temperature to ~180 °C. Heating is restored to the reaction flask and the temperature is gradually raised to 230–260 °C.

Aliquots of the reaction solution are removed at regular intervals (5–10 min) and absorption spectra taken to monitor the growth of the nanocrystallites. The best quality samples are prepared over a period of a few hours of steady growth by modulating the growth temperature in response to changes in the size distribution as estimated from the absorption spectra. The temperature is lowered in response to a spreading of the size distribution and increased when growth appears to stop. When the desired absorption characteristics are observed, a portion of the growth solution is transferred by cannula and stored in a vial. In this way, a series of sizes ranging from ~15 to 115 Å in diameter can be isolated from a single preparation.

CdTe nanocrystallites are prepared by Method 1 with TOPTe as the chalcogen source, an injection temperature of ~240 °C, and growth temperatures between ~190 and ~220 °C.

Method 2. A second route to the production of CdE (E = S, Se, Te) nanocrystallites replaces the phosphine chalcide precursors in Method 1 with (TMS)₂S, (TMS)₂Se, and (BDMS)₂Te, respectively. Growth temperatures between ~290 and ~320 °C were found to provide the best CdS samples. The smallest (~12 Å) CdS, CdSe, and CdTe species are produced under milder conditions with injection and growth carried out at ~100 °C.

Isolation and Purification of Crystallites. A 10-mL aliquot of the reaction solution is removed by cannula and cooled to ~60 °C, slightly above the melting point of TOPO. Addition of 20 mL of anhydrous methanol to the aliquot results in the reversible flocculation of the nanocrystallites. The flocculate is separated from the supernatant by centrifugation. Dispersion of the flocculate in 25 mL of anhydrous 1-butanol followed by further centrifugation results in an optically clear solution of nanocrystallites and a gray precipitate containing byproducts of the reaction. Powder X-ray diffraction and energy dispersive X-ray analysis indicate these byproducts consist mostly of elemental Cd and Se. This precipitate is discarded. Addition of 25 mL of anhydrous methanol to the supernatant produces flocculation of the crystallites and removes excess TOP and TOPO. A final rinse of the flocculate with 50 mL of methanol and subsequent vacuum drying produces ~300 mg of free flowing TOP/TOPO capped CdSe nanocrystallites. The resulting powder is readily dispersed in a variety of alkanes, aromatics, long-chain alcohols, chlorinated solvents, and organic bases (amines, pyridines, furans, phosphines).

Size-Selective Precipitation. Purified nanocrystallites are dispersed in anhydrous 1-butanol forming an optically clear solution. Anhydrous methanol is then added dropwise to the dispersion until opalescence persists upon stirring or sonication. Separation of supernatant and flocculate by centrifugation produces a precipitate enriched with the largest crystallites in the sample. Dispersion of the precipitate in 1-butanol and size-selective precipitation with methanol is repeated until no further sharpening of the optical absorption spectrum is noted. Size-selective precipitation can be carried out in a variety of solvent/nonsolvent pairs, including pyridine/hexane and chloroform/methanol.

Surface Exchange. Crystallite surface derivatization can be modified by repeated exposure to an excess of a competing capping group. Heating to ~60 °C a mixture of ~50 mg of TOPO/TOP capped crystallites and 5–10 mL of pyridine gradually disperses the crystallites in the solvent.

(5) Zingaro, R. A.; Steeves, B. H.; Irgolic, K. *J. Organomet. Chem.* 1965, 4, 320.

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Treatment of the dispersion with excess hexane results in the flocculation of the crystallites which are then isolated by centrifugation. The process of dispersion in pyridine and flocculation with hexane is repeated a number of times to produce crystallites which disperse readily in pyridine, methanol, and aromatics but no longer disperse in aliphatics.

Optical Characterization. Optical absorption spectra were collected at room temperature on a Hewlett-Packard 8452 diode array spectrometer using 1-cm quartz cuvettes. Samples were prepared by dispersing washed CdSe nanocrystallites in hexane. Luminescence experiments were carried out on a SPEX Fluorolog-2 spectrometer with use of front face collection with 500-μm slits. Estimates of quantum yield were obtained by comparing the integrated emission from Rhodamine 640 in methanol and that of 35 Å diameter CdSe nanocrystallites dispersed in hexane. Concentrations of both were adjusted to provide optical densities of 0.30 at 460 nm in matched 1-mm quartz cuvettes. Fluorescence spectra were collected between 480 and 800 nm at room temperature with 460-nm excitation.

Transmission Electron Microscopy. A Tescan EM002B electron microscope operating at 200 kV was used for transmission electron microscopy (TEM). Imaging was carried out in bright field with an objective aperture selected to permit lattice imaging of the (100), (002), and (101) Wurtzite planes. Copper grids (300 mesh) coated with a ~50 Å amorphous carbon film were purchased from Ernest Fullam. Samples were prepared by placing a drop of a dilute pyridine dispersion of nanocrystallites on the surface of a grid, waiting for ~1 min, and then wicking away the solution. The coverage level of crystallites was adjusted by varying the initial dispersion concentration and the contact time.

X-ray Powder Diffraction. Powder X-ray diffraction spectra were collected on a Rigaku 300 Rotaflex diffractometer operating in the Bragg configuration using Cu K α radiation. The accelerating voltage was set at 250 kV with a 200 millamp flux. Scatter and diffraction slits of 0.50° and a 0.15-mm collection slit were used. Samples for X-ray diffraction were prepared from ~500 mg of thoroughly washed and dried nanocrystallite powder. The free-flowing powders were pressed at 5000 psi to form 0.3 in. diameter pellets with mirror flat surfaces.

III. Results and Discussion

The production and phenomenology of monodisperse lyophobic colloids has been investigated since Faraday's production of gold sols in 1857.⁶ Classic work by La Mer and Dinegar⁷ has shown that the production of a series of monodisperse lyophobic colloids depends on a temporally discrete nucleation event followed by controlled growth on the existing nuclei. Temporally discrete nucleation in our synthesis is attained by a rapid increase in the reagent concentrations upon injection, resulting in an abrupt supersaturation which is relieved by the formation of nuclei and followed by growth on the initially formed nuclei.

The work of Steigerwald and co-workers on the use of organometallic precursors in the solution-phase synthesis of bulk and nanocrystalline materials provides guidance in our selection of reagents.^{3a,b,8} Me₂Cd is chosen as the Cd source and (TMS)₂E (E = S, Se, Te) or TOPSe and TOPTe are selected as chalcogen sources with TOPSe and TOPTe preferred due to their ease of preparation and their stability. Me₂Cd and (TMS)₂E reagents have been shown to undergo dealkylsilylation in a variety of solvents as a route to the production of bulk materials.⁹ Trimethylphosphine telluride is known as a good source of Te⁶⁺.⁹ Mixed phosphine/phosphine oxide solutions have previously been found to be good solvents for the high-temperature growth and annealing of CdSe crystallites.^{2d,e,10} The coordinating solvent plays a crucial role in controlling the growth process, stabilizing the resulting colloidal dispersion, and electronically passivating the semiconductor surface.

Nucleation and Growth. Injection of reagents into the hot reaction pot results in a short burst of homogeneous nucleation.

(6) Overbeek, J. Th. G. *Adv. Colloid Interface Sci.* 1982, 15, 151.

(7) LaMer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* 1930, 52, 4847.

(8) Stuczynski, S. M.; Brennan, J. G.; Steigerwald, M. L. *Inorg. Chem.* 1989, 28, 4431.

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The depletion of reagents through nucleation and the sudden temperature drop associated with the introduction of room temperature reagents prevents further nucleation. Gently reheating allows slow growth and annealing of the crystallites. Crystallite growth appears consistent with "Ostwald ripening", where the higher surface free energy of small crystallites makes them less stable with respect to dissolution in the solvent than larger crystallites. The net result of this stability gradient within a dispersion is slow diffusion of material from small particles to the surface of larger particles.¹¹ Reiss has shown how growth by this kind of transport can result in the production of highly monodisperse colloidal dispersions from systems that may initially be polydisperse.¹²

Both the average size and the size distribution of crystallites in a sample are dependent on the growth temperature, consistent with surface free energy considerations. The growth temperature necessary to maintain steady growth increases with increasing average crystallite size. As the size distribution sharpens, the reaction temperature must be raised to maintain steady growth. Conversely, if the size distribution begins to spread, the temperature necessary for slow steady growth drops. Size distributions during growth are crudely estimated from absorption line widths (typically 50 nm fwhm). Modulation of the reaction temperature in response to changes in the absorption spectrum allows the maintenance of a sharp size distribution as the sample grows.

The Ostwald ripening process accentuates any kinetic or thermodynamic "bottleneck" in the growth of crystallites. As a bottleneck is approached (e.g. a closed structural shell), sharpening of the sample size distribution reduces the thermodynamic driving force for further growth. Sharpening in the absorption features as the average particle size approaches 12, 20, 35, 45, and 51 Å in diameter may point to the presence of such bottlenecks.

Capping groups present a significant steric barrier to the addition of material to the surface of a growing crystallite, slowing the growth kinetics. The TOP/TOPO solvent coordinates the surfaces of the crystallites and permits slow steady growth at temperatures above 280 °C. Replacing the octyl chains with shorter groups reduces the temperature for controlled growth. Mixed alkylphosphine/alkylphosphine oxide solvents with butyl, ethyl, and methyl groups show uncontrolled growth at 230, 100, and 50 °C, respectively. Steady controlled growth results in highly monodisperse particles of consistent crystal structure and allows size selection by extracting samples periodically from the reaction vessel.

A wealth of potential organometallic precursors and high boiling point coordinating solvents exist. Although phosphine/phosphine oxide have been found to provide the most controlled growth conditions, injections of reagents into hot pyridines, tertiary amines, and furans all allow production of nanocrystallites.

We are beginning the extension of this synthetic method to the production of ZnE and HgE materials using diethylzinc and dibenzylmercury as group II sources. Growth conditions have not yet been optimized to provide sample quality comparable to that of CdE materials.

Colloid Stabilization and Size-Selective Precipitation. Lycophobic colloidal particles attract each other by van der Waals forces. The attraction is strong due to the near additivity of forces between pairs of unit cells in different particles.¹³ Colloids remain stable with respect to aggregation only if there exists a repulsive force of sufficient strength and range to counteract the van der Waals attraction. Chemisorption of amphiphilic species on the surface of the particles gives rise to a steric barrier to aggregation. The dispersions of CdSe nanocrystallites are

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(12) Reiss, H. *J. Chem. Phys.* 1951, 19, 482.

(13) Sato, T.; Ruchi, R. *Stabilization of Colloidal Dispersions by Polymer Adsorption*; Marcel Dekker: New York, 1980; pp 46-51.

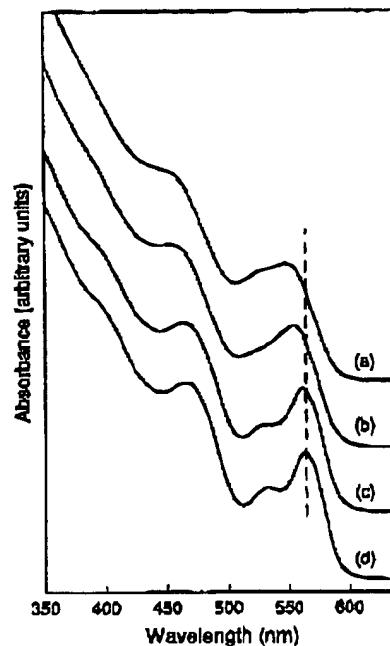


Figure 1. Example of the effect of size-selective precipitation on the absorption spectrum of ~37 Å diameter CdSe nanocrystallites. (a) Room temperature optical absorption spectrum of the nanocrystallites in the growth solution before size-selective precipitation. (b) Spectrum after one size-selective precipitation from the growth solution with methanol. (c) Spectrum after dispersion in 1-butanol and size-selective precipitation with methanol. (d) Spectrum after a final size-selective precipitation from 1-butanol/methanol.

sterically stabilized by a lyophobic coat of alkyl groups anchored to the crystallite surface by phosphine oxide/chalcocide moieties. The efficiency of the steric stabilization is strongly dependent on the interaction of the alkyl groups with the solvent. Gradual addition of a nonsolvent can produce size-dependent flocculation of the nanocrystallite dispersion. This phenomenon is exploited in further narrowing the particle size distribution.

The addition of methanol increases the average polarity of the solvent and reduces the energetic barrier to flocculation. The largest particles in a dispersion experience the greatest attractive forces. These large particles have a higher probability of overcoming the reduced barrier and are thus enriched in the flocculate produced. The removal of a specific subset of particles from the initial size distribution narrows the size distribution of both supernatant and precipitate. Depending on the cap molecule, a number of solvent/nonsolvent systems can be used for size-selective precipitation (e.g. hexane/ethanol, chloroform/methanol, pyridine/hexane, etc....).

Figure 1 illustrates the result of size-selective precipitation. Spectrum a shows the optical absorption of the initial growth solution. The broad absorption features correspond to a sample with an average size of $35 \text{ \AA} \pm 10\%$ (sized by TEM). Slow addition of methanol results in the flocculation of the larger particles in the distribution which give spectrum b after dispersing in 1-butanol. Titration of methanol in sample b again produces flocculation of the larger particles, giving spectrum c upon dispersion in 1-butanol. A final size-selective precipitation from 1-butanol yields a sample with optical absorption d and with an average size of $\sim 37 \text{ \AA} \pm 5\%$. Spectrum d is dramatically sharpened relative to that of the initial growth solution and reveals transitions at 530 and ~ 400 nm which were previously cloaked by polydispersity. For the fractionation process to work well it is crucially important that the shape and surface derivatization of the initial crystallites be uniform and that the initial polydispersity in size be relatively small.

Synthesis of CdE Semiconductor Nanocrystallites

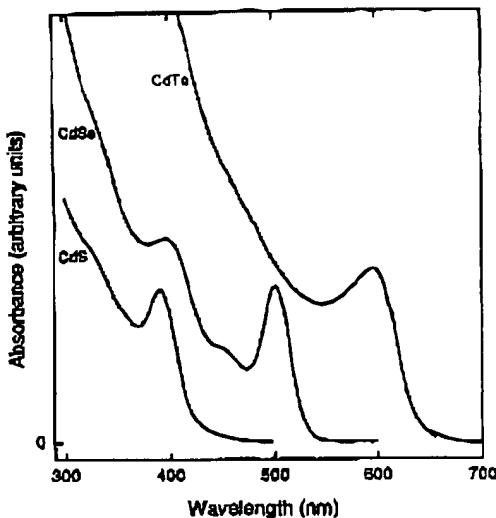


Figure 2. Room temperature optical absorption spectra of $\sim 20\text{--}30\text{ \AA}$ diameter CdS, CdSe, and CdTe crystallites.

Surface Exchange. Preliminary studies of surface exchange have been used to tailor the compatibility of crystallites with a variety of solvents. Exposure of purified crystallites to a large excess of pyridine begins the exchange of the surface cap. Addition of solvents compatible with TOPO and TOP but incompatible with the new cap results in the flocculation of the crystallites and the removal of displaced TOP and TOPO species. The repeated dispersion in pyridine and isolation with alkanes drives the surface exchange with mass action. Crystallites capped with pyridine are dispersible in polar solvents and aromatics but not aliphatics. Surface exchange results in a slight decrease in average crystallite size and a small broadening of the size distribution, probably due to the loss of species containing Cd and Se. Sharp optical features can be recovered by size-selective precipitation from pyridine with the titration of hexane. Crystallites can be stabilized in a variety of solvents with a range of functionalized caps. There is obvious potential for customizing photochemical activity of these robust chromophores through manipulation of their immediate chemical environment.

Optical Properties. The absorption spectra of $\sim 20\text{--}30\text{ \AA}$ diameter CdS, CdSe, and CdTe nanocrystallites samples are shown in Figure 2. All three clearly show the effect of quantum confinement. CdS, CdSe, and CdTe absorptions are shifted dramatically from their 512, 716, and 827 nm bulk band gaps, respectively. The CdSe spectrum shows three clearly resolved transitions while the CdS and CdTe samples show less structure. We do not believe the difference in quality of the optical spectra reflects any fundamental material limitations but rather the amount of effort spent in optimizing the growth conditions for each material.

Figure 3 shows the evolution of the optical spectrum with size in a series of room temperature absorption spectra for CdSe crystallites ranging from ~ 12 to 115 \AA in diameter. The series spans a range of sizes from nearly molecular species containing fewer than 100 atoms to fragments of the bulk lattice containing more than 30 000 atoms. Figure 4 compares the experimentally observed HOMO LUMO gap as a function of particle size with the prediction of the simple effective mass approximation with the Coulomb interaction treated in first-order perturbation.¹⁴ All particle sizes were determined by TEM and confirmed by X-ray line-shape analysis. Although experiment and theory agree reasonably well at large sizes, the simple theory diverges from the experimental values for small sizes as expected from the non-parabolicity of the bands at higher wave vectors and the finite potential barrier at the surface of the particles. Lippens and

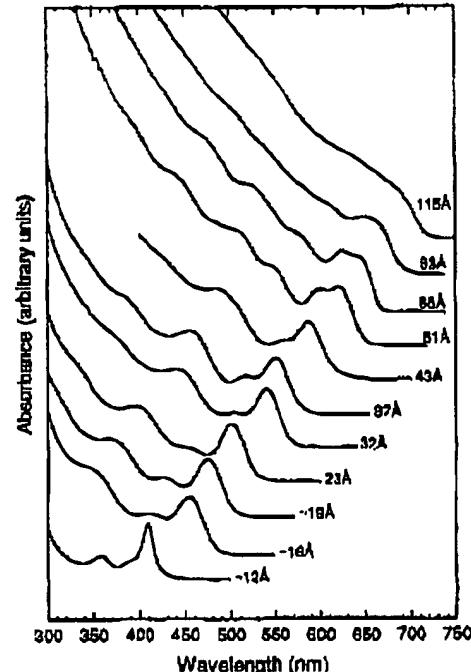
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Figure 3. Room temperature optical absorption spectra of CdSe nanocrystallites dispersed in hexane and ranging in size from ~ 12 to 115 \AA .

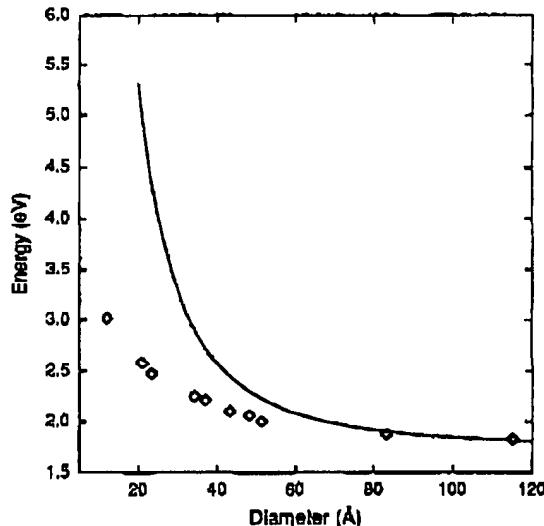


Figure 4. HOMO LUMO transition energy of CdSe crystallites as a function of size (diamonds) compared with the prediction of the effective mass approximation (solid line).

Lannoo¹⁴ have shown that tight binding calculations can yield better agreement for these smaller sizes.

Figure 5 shows the room temperature photoluminescence spectrum of a sample of 35 \AA diameter CdSe crystallites and compares it with the absorption spectrum. The luminescence quantum yield for this sample is $\sim 9.6\%$ relative to Rhodamine 640 at room temperature. The line width in emission is equal to that in absorption, with the peak of the emission shifted 4 nm to the red of the absorption maximum. This shift is the result of a combination of relaxation into shallow trap states and the size distribution.^{2a} No deep trap emission was detected.

(14) (a) Lippens, P. E.; Lannoo, M. *Phys. Rev. B* 1989, 39, 10935. (b) Lippens, P. E.; Lannoo, M. *Mater. Sci. Eng. B* 1991, 9, 485.

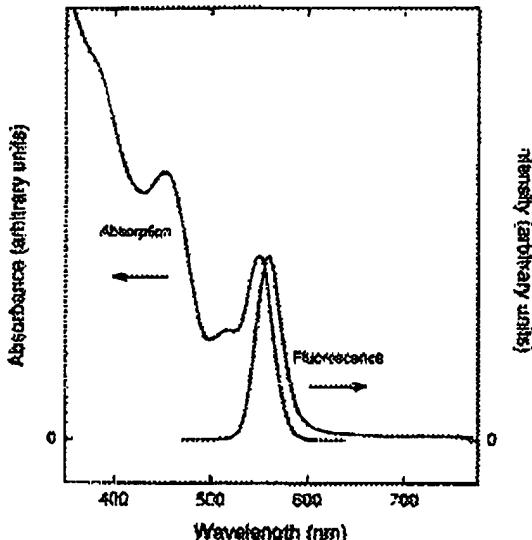


Figure 5. Typical room temperature band edge luminescence and absorption spectra for 35 Å diameter CdSe crystallites. No deep trap luminescence is detected.

The sharp absorption features suggest highly monodisperse samples. High quantum yields and narrow emission line widths indicate growth of crystallites with few electronic defect sites. The sharp luminescence is a dramatic example of the efficiency of the capping group in electronically passivating the crystallites. The capping groups also protect the individual crystallites from chemical degradation yielding robust systems. Samples stored in the original growth solution still show strong, sharp emission after storage for more than a year.

These room temperature optical experiments, carried out on common laboratory equipment, demonstrate the benefits of high-quality samples and point to the potential of more sophisticated optical studies on these samples.

Transmission Electron Microscopy. Transmission electron microscopy allows imaging of individual crystallites and the development of a statistical description of the size and shape of the particles in a sample. High magnification imaging with lattice contrast allows the determination of individual crystallite morphology.¹³

Imaging at 350×10^3 times magnification with moderate crystallite coverage allows careful size measurements of 30 to 50 individual nanocrystallites on a single image and shows that the particles are not aggregated. Figure 6 shows a collection of slightly prolate CdSe nanocrystallites averaging $35.0 \text{ \AA} \pm 5\%$ in the direction of the (002) wurtzite axis and $30 \text{ \AA} \pm 6\%$ perpendicular to the (002) axis. Particles with the (002) axis perpendicular to the grid are identified by a characteristic hexagonal pattern in atom imaging and are nearly circular in cross section. Particles oriented in other directions appear slightly oblong. The analysis of samples ranging from ~ 20 up to 115 \AA indicates slightly prolate particles with aspect ratios between 1.1 and 1.3.¹⁶ Samples generally have standard deviations $<5\%$ in the long axis and $<6\%$ in the shorter dimension. All diameters quoted in this paper are a measure of the major axis. This axis is more precisely measured because it is easier to distinguish the edges of a crystallite in the (002) direction rather than perpendicular to it. The loss of contrast at the surface of the crystallite makes the assignment of the final atomic plane uncertain and introduces the greatest source of experimental error. The standard deviation values are thus actually measurement limited with an experimental uncertainty of one atomic plane per crystallite.



Figure 6. TEM image taken in bright field with lattice contrast shows a collection of slightly prolate particles. The elongated (002) axis measures $35.0 \text{ \AA} \pm 5\%$ while the perpendicular axis measures $30 \text{ \AA} \pm 6\%$. The particles are well dispersed and not aggregated.

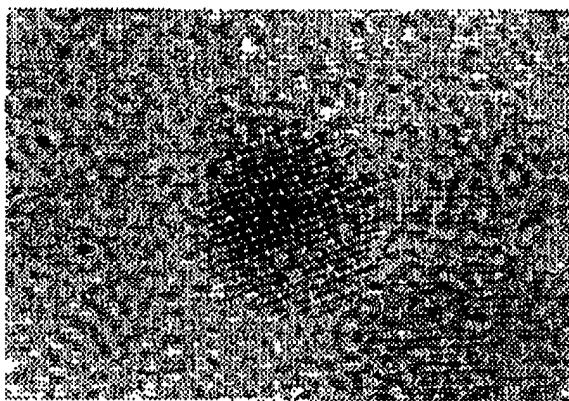


Figure 7. An 80 Å diameter CdSe crystallite imaged in bright field with atom contrast shows the presence of stacking faults in the (002) direction.

High-magnification imaging (390×10^3 to 1×10^6) allows the detection of planar disorder in individual crystallites. Figure 7 shows an 80 Å diameter CdSe nanocrystallite atom imaged perpendicular to the (100) and (002) axes. Planar disorder along the (002) axis is clearly observed. Figure 8 shows a $\sim 110 \text{ \AA}$ diameter crystallite with a 1.33 aspect ratio and four clear stacking faults in the (002) direction (the left particle). A neighboring crystallite displays the hexagonal atom imaging pattern resulting from imaging along the (002) axis. No planar disorder is detectable in this projection. The analysis of a series of samples leads to some general results. The (002) planes (perpendicular to the long axis) show little disorder while loss of lattice image contrast is most commonly seen in the (100) planes (parallel to the long axis) and in the (101) planes. This loss of contrast is believed to result from the presence of stacking faults along the (002) direction. These stacking faults are the predominant form

(13) Kibaborg, L. *Prog. Solid State Chem.* 1990, 20, 101.

(16) Similar aspect ratios have been previously observed. See: Rossetti, R.; Elliston, J. L.; Gibson, J. M.; Brus, L. R. *J. Chem. Phys.* 1994, 90, 4464.

Synthesis of CdE Semiconductor Nanocrystallites

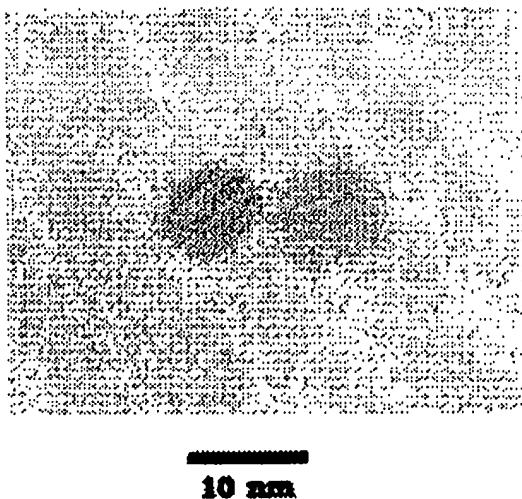


Figure 8. The crystallite on the left (~ 110 Å) shows a loss of lattice contrast in the (101) planes pointing to the presence of 4 stacking faults along the (002) direction. The crystallite is prolate with an aspect ratio of ~ 1.5 . The crystallite on the right presents a projection perpendicular to the (002) direction and displays the hexagonal atom imaging characteristics of the wurtzite structure.

of disorder in bulk II-VI materials.^{17a} Chadderton *et al.* also use changes in lattice contrast to identify individual stacking faults in a series of 100-nm II-VI thin films.¹⁸

There is a broad distribution in the position and frequency of stacking faults within each sample. Statistically more stacking faults are observed near the center of crystallites which may point to an increased probability of faulting early in the growth. It is also possible that greater contrast in the central region improves the detection of faults. The wavy lattice patterns of individual faulted crystallites seen in TEM can be qualitatively reproduced in computer generated atom images of crystallites by introducing stacking faults along the (002) axis.

TEM allows not only the investigation of the morphology of individual crystallites but also the observation of ordering of crystallites into secondary structures. Two-dimensional hexagonal close packing begins to form (Figure 9) at relatively high coverage levels. The tailoring of mixed solvents in the fashion permitting selective precipitation may allow more controlled growth of such secondary structures.

Selected area electron diffraction patterns confirm a predominantly wurtzite structure. Although a common technique, selected area diffraction is not emphasized in our structural analysis. Bright field images indicate that our crystallites are not randomly oriented on the TEM grid but exhibit a tendency to orient with their long axis parallel to the carbon surface. The nonstatistical distribution of crystal orientations can greatly impair the interpretation of electron diffraction line shapes. Electron microdiffraction may provide an appropriate alternative to selected area diffraction in these systems.¹⁹

X-ray Diffractee. Unlike TEM, X-ray powder diffraction probes a large number of crystallites that are statistically oriented. Samples are prepared as dense pellets free of any amorphous binder to provide a strong signal with low background. The pellets disperse readily in a variety of solvents with no apparent change in the absorption spectra.

Samples of CdS, CdSe, and CdTe crystallites all exhibit a predominantly wurtzite crystal structure with the lattice spacing

(17) Aver, M.; Prenter, J. S. *Physics and Chemistry of II-VI Compounds*; North Holland: Amsterdam, 1967; pp 144 (a) and 132 (b).

(18) Chadderton, L. T.; Fitzgerald, A. G.; Yaffe, A. D. *Nature* 1983, 298, 573.

(19) Loretto, M. H. *Electron beam analysis of Materials*; Chapman and Hall: London, 1986; pp 50-51.



Figure 9. A near monolayer of 51 Å diameter CdSe crystallites showing short-range hexagonal close packing.

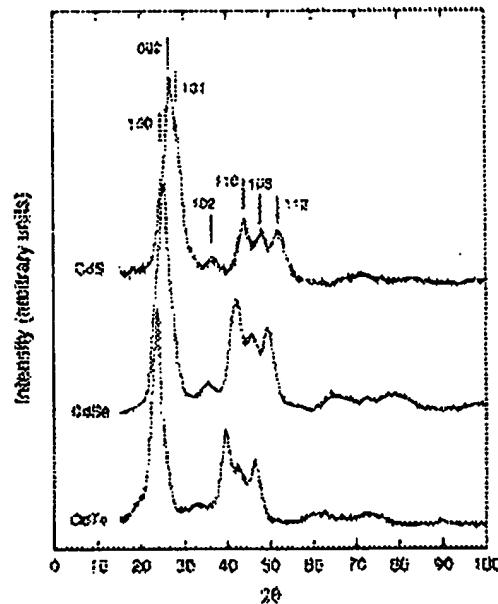


Figure 10. Powder X-ray diffraction spectra of ~ 35 Å CdS, CdSe, and CdTe crystallites. The positions of bulk reflections for wurtzite CdS are indicated.

of the bulk materials (Figure 10). Bulk crystals of CdS and CdSe commonly exhibit the wurtzite structure when prepared at high temperature. The hexagonal modification of CdTe has been observed in thin films although to our knowledge it has not been seen in bulk crystals.^{17b}

Experimental X-ray powder diffraction spectra for CdSe crystallites ranging from ~ 12 to 115 Å in diameter are displayed in Figure 11. Spectra show evidence of finite size broadening in all reflections.²⁰ Excessive attenuation and broadening in the

(20) Guinier, A. *X-Ray Diffraction*; W. H. Freeman: San Francisco, 1963; pp 122-149 (a) and 226-237 (b).

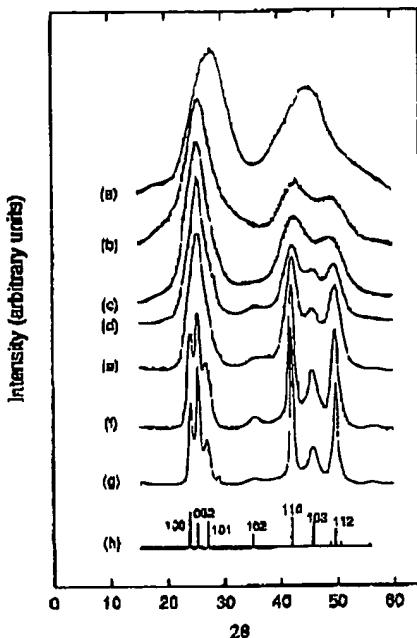


Figure 11. Powder X-ray diffraction spectra of (a) 12, (b) 18, (c) 20, (d) 37, (e) 42, (f) 83, and (g) 115 Å diameter CdSe nanocrystallites compared with the bulk wurtzite peak positions (b).

(102) and (103) reflections are characteristic of stacking faults along the (002) axis.²⁰ The diffraction pattern of the ~12 Å diameter species appears dramatically different from that of the other sizes. These small clusters possess too few atoms to define a core crystal structure, making the distinction between wurtzite and zincblende meaningless. The dramatic change in their diffraction features may indicate significant surface reconstruction or contributions from the capping groups to the diffraction pattern. Proper structural analysis of these nearly molecular species will require the isolation of materials as single crystals as has been achieved with CdS.²¹

Structural Simulations. Modeling of nanocrystallite samples as collections of monodisperse spherical single crystals with ideal surface termination is appealing but may potentially be misleading. In this section we develop a working description of average crystallite morphology using a combination of experimental and computer simulated X-ray diffraction patterns and parameters which are consistent with other independent structural probes.

The combination of finite size and defect broadening results in a convolution of peaks in the X-ray diffraction spectra. Direct observation of peak positions and peak widths are thus unreliable measures of lattice spacing and crystallite size. But structural information can be extracted by using TEM and EXAFS²² observations to guide in fitting the experimental X-ray diffraction spectra. Previous studies of the X-ray powder patterns of CdSe nanocrystallites have demonstrated the sensitivity of spectra to the presence of planar disorder and thermal effects.¹⁰ These studies are extended here over a range of sizes. The importance of crystallite shape, the question of lattice contractions, and probable surface disorder are investigated.

(21) Herron, N.; Calabrese, J. C.; Farneth, W. E.; Wang, Y. *Science* 1993, 259, 1426. Our smallest CdS particles have optical spectra identical with those in this reference. We believe the smallest CdSe particles in our series are the CdSe analogue to the CdS particles crystallized in this work.

(22) (a) Marcus, M. A.; Flood, W.; Steigerwald, M. L.; Brus, L. E.; Bawendi, M. G. *J. Phys. Chem.* 1991, 95, 1572. (b) Marcus, M. A.; Brus, L. E.; Murray, C. B.; Bawendi, M. G.; Prasad, A.; Alivisatos, A. P. *Nanostruct. Mater.* 1992, 7, 323.

Fits to experimental spectra employ a discrete form of the Debye equation:²³

$$I(S) = I_0 \frac{f^2(S)}{2\pi S} \sum_k \frac{p(r_k)}{r_k} \sin(2\pi r_k S)$$

where $I(S)$ is the diffracted intensity, I_0 is the incident intensity, $f(S)$ is the scattering factor, and S is the scattering parameter [$S = 2 \sin(q)/\lambda$ for X-rays of wavelength λ diffracted through angle q]. The sum is over all discretized interatomic distances r_k , and $p(r_k)$ is the number of times a given interatomic distance r_k occurs. Since the number of discrete interatomic distances in an ordered structure grows much more slowly than the total number of distances, the discrete form of the equation is significantly more efficient for large crystallites.

Atomic coordinates are obtained by systematically generating atomic positions for a bulk crystalline lattice and retaining only those atoms falling within a defined ellipsoid. EXAFS studies²² support the use of bulk bond lengths (2.63 Å for CdSe). The dimensions for the ellipsoid are taken from TEM measurements of average size and shape. Planar disorder along the (002) axis is reproduced by creating a collection of coordinate files with a broad distribution of stacking faults about the center of the crystallites. The resulting spectra are statistically weighted and summed to create a crystallite sample distribution with a defined average defect density. Thermal effects are simulated by the introduction of a Debye-Waller factor.²⁴ A constant Debye-Waller factor is used based on a mean-square displacement of 0.04 Å² for each atom, consistent with EXAFS studies²² which find bulk Debye-Waller factors. The Debye-Waller factor does not change peak positions and only affects peak intensities through an exponential damping as S increases. The broad backgrounds in the experimental diffraction spectra are subtly influenced by the combined effects of experimental geometry, variable absorption of X-rays, contributions from incoherent scattering, thermal effects (Debye-Waller term), and scattering from the capping groups. Rigorous correction of the background from these contributions requires a knowledge of sample properties not presently available. A constant background chosen to best fit the relative intensity of the (110) reflection for 37 Å crystallites is added to all simulated spectra to crudely compensate for the experimental contributions to the background. This background is not important in our analysis which concentrates on the diffraction features.

Figure 12 compares calculated spectra of 1000 atom spherical CdSe particles (~37 Å diameter) with the experimental powder pattern of a similarly sized sample. The spectra of defect free zincblende (a) and wurtzite (b) crystallites do not reproduce the overall shape of experimental spectrum (d), especially in the region between the (110) and (112) peaks. The introduction of a single stacking fault near the center of an otherwise wurtzite crystallite greatly improves the fit (spectrum c) by broadening the (103) peak.

The (110) spacing is present in both the wurtzite and zincblende structures and is thus unaffected by the presence of stacking faults along the (002) axis. This spacing also has reasonable separation from neighboring reflections. Crude estimates of particle size based on the Scherer analysis of peak widths should employ the width of the (110) feature rather than the convolution of the (100), (002), and (101) reflections found in the first diffraction feature. This convolution is easily confused with the (111) zincblende reflection, and using it to estimate particle size would underestimate the coherence length. The agreement in the width and shape of the (110) feature between our simulated spectra using crystallite dimensions based on TEM measurements.

(23) Hall, B. D.; Monot, R. *Comput. Phys.* 1991, 5, 414.

(24) Vettulano, J. F.; Guar, S. P.; Mitra, S. S. *Phys. Rev. B* 1972, 5, 2360.

Synthesis of CdS Semiconductor Nanocrystallites

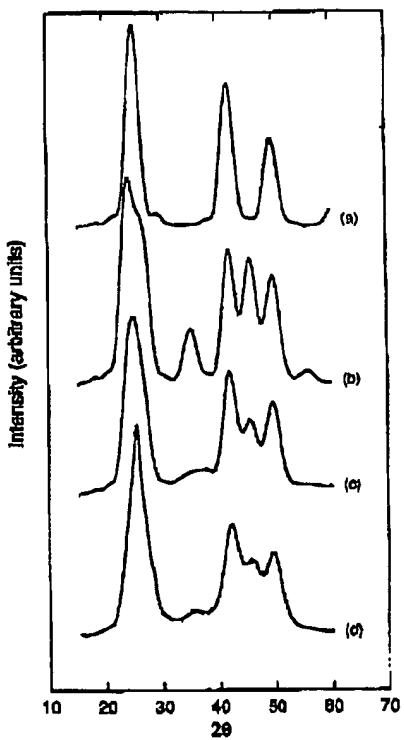


Figure 12. Simulated X-ray powder diffraction spectra for 35 \AA diameter spherical nanocrystallites: (a) pure zincblende, (b) pure wurtzite, (c) wurtzite with one stacking fault. (d) Experimental powder spectrum of $\sim 35\text{ \AA}$ diameter crystallites.

and our experimental spectra confirms crystallite size and indicates that structural defects must be coherent defects (e.g. stacking faults).

Figure 13 highlights the sensitivity of the diffraction spectrum to crystallite shape. The experimental spectrum of a sample of CdSe nanocrystallites containing on average $\sim 10\,000$ atoms ($\sim 80\text{ \AA}$ diameter) is compared with simulations. The best fits obtained assuming spherical particles (spectrum a) and prolate particles with an aspect ratio of 1.3 in the (002) direction (spectrum b) are shown. Each simulation has an average defect density of 3 stacking faults per crystallite to fit the region of the (103) peak. While the (100) feature is more intense than the (002) peak in bulk CdSe and in the simulated spectrum of spherical particles, the opposite is true for our crystallites and in the simulation of prolate particles. The elongated particles have a larger number of (002) planes, making that peak the dominant reflection in the first diffraction feature. The greater coherence length in that direction results in the narrowing of (002) reflection and a smaller overlap with the neighboring (100) and (101) reflections. Inclusion of the prolate nature of the particles, observed in TEM, is essential for reproducing the shape of the convolution of the (100), (002), and (101) reflections. We fix the aspect ratio at ~ 1.3 for the simulations of the other sizes to minimize the number of floating parameters.

The first broad diffraction feature ($2\theta \sim 25^\circ$) appears to shift to higher scattering angles with decreasing particle size (Figure 11). An isotropic lattice contraction of a few percent due to surface tension has been proposed as a possible explanation for similar observations in CdS nanocrystallites.²⁵ EXAFS data²² however yield average bond lengths which are essentially identical with those in the bulk even for the smallest crystallites. In fact, even the small $\sim 12\text{ \AA}$ CdS clusters recently crystallized by Herron

(25) (a) Wang, Y.; Herron, N. *Phys. Rev. B* 1990, 42, 7233. (b) Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. *Science* 1992, 256, 1425. (c) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* 1992, 114, 5221.

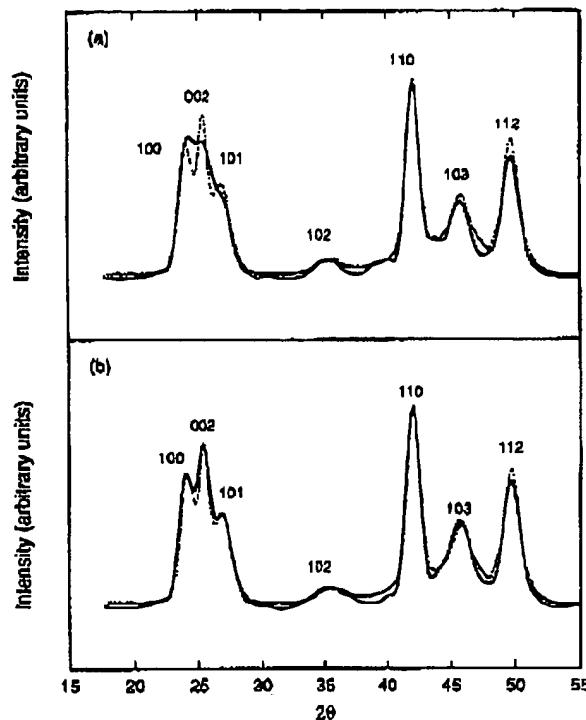


Figure 13. Experimental X-ray powder diffraction spectrum of $\sim 80\text{ \AA}$ diameter ($\sim 10\,000$ atoms) crystallites (dotted line) compared with computer simulations (solid line) of (a) spherical and (b) prolate particles [aspect ratio of 1.3 along the (002) direction]. Three stacking faults on average and bulk lattice constants are used.

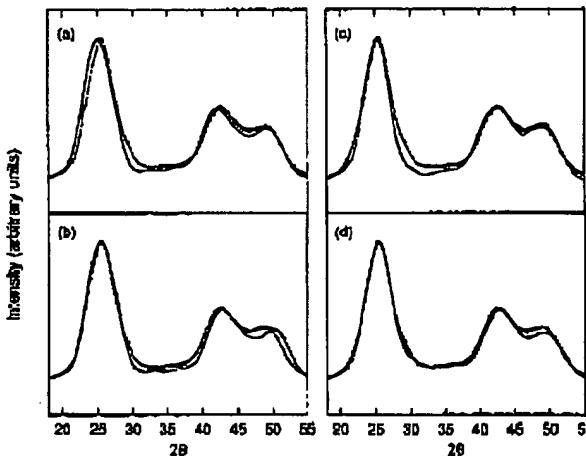


Figure 14. Experimental X-ray powder diffraction spectrum of $\sim 20\text{ \AA}$ (~ 275 atoms) diameter crystallites (dotted line) compared with a series of computer simulations of wurtzite crystallites containing 275 atoms with one stacking fault per crystallite in the (002) direction (solid lines). (a) Spherical particles with bulk lattice parameters, (b) spherical particles with 2% isotropic lattice contraction, (c) prolate particles [aspect ratio of 1.3 along the (002) axis] with bulk lattice parameter, (d) moderate surface disorder added to the prolate particles of part c.

et al.²¹ only show a bond contraction of $\sim 0.5\%$ compared to the bulk. This apparent contradiction can be resolved in our samples by properly taking crystallite shape into account. Figure 14a compares the experimental spectrum of small CdSe crystallites containing ~ 275 atoms ($\sim 20\text{ \AA}$ diameter) to the simulated spectrum of spherical particles with a bulk lattice parameter, showing a clear shift of the first experimental peak to higher angles. Figure 14b compares the same experimental spectrum with the simulated spectrum of spherical particles with a lattice

parameter contracted by 2%. A constant defect density of one stacking fault/crystallite is used in both simulations to fit the valley between the (110) and (112) peaks. The 2% contraction is designed to reproduce the position and general shape of the first diffraction feature but results in a poor fit at higher angles. Observation of a shift in the first peak is not enough to prove a lattice contraction. The higher peaks must also shift. Figure 14c shows the effect of putting an aspect ratio on the crystallites. The experimental pattern is compared with the simulated spectrum of prolate particles having an aspect ratio of ~ 1.3 in the (002) direction, a bulk lattice parameter, and one stacking fault per crystallite. The introduction of crystallite shape uniformly improves the fit without requiring a major lattice contraction. The prolate shape results in the prominence of the (002) reflection, skewing the first diffraction feature to higher scattering angles. This effect is especially important for smaller crystallites which have few planes and where a single extra plane has a tremendous effect on the intensity and width of the diffraction feature for that direction. Thus, for the same aspect ratio, small crystallites exhibit a larger apparent shift than larger crystallites. Fits with prolate crystallites reproduce the position of the peaks and the general shape of the spectrum but show a lack of intensity in a broad region between $2\theta \sim 27^\circ$ and 33° compared to the experimental data.

TEM observations suggest poorly resolved facets and the presence of a potentially reconstructed surface layer limiting the accuracy of measurements to no better than one atomic plane. The presence of surface disorder is simulated in our studies by the relaxation of all atoms lacking their full coordination shell. The poorly defined crystal surfaces make the choice of a specific reconstruction difficult. Studies by Duke and Wang on clean II-VI surfaces in high vacuum have established general mechanisms for reconstruction on cleavage faces.²⁴ A general tendency for a bond length conserving rotation of surface II-VI pairs results in the cation relaxing into the surface while the anion is pushed out of the plane. We retain the character of these relaxations in our simulations by radially translating all surface cations 0.40 \AA toward the cylindrical axis of the crystallite. The surface anions are translated outward by 0.20 \AA . The magnitude of the relaxation is comparable to that of Duke and Wang²⁴ and it is chosen to provide the best fit to the experimental data. The average bond length is kept to within $\pm 0.005\text{ \AA}$ of the bulk value for consistency with EXAFS experiments which show negligible bond length contractions.²⁵ Figure 14d shows that agreement with experimental spectra can be improved by the introduction of such surface disorder. The choice of the relaxation is not unique and is not an attempt to define a specific surface structure, rather it is to show that surface disorder is compatible with the experimental X-ray data. We fix the amount of surface disorder to that used for the 20-\AA particles above since we do not expect it to be strongly size dependent. Effects of surface disorder become imperceptible as the crystallite size increases ($>50\text{ \AA}$).

Figure 15 shows the experimental spectrum of a sample of 37 \AA diameter crystallites (~ 1000 atoms) compared with a simulation for crystallites with a defect density of 1.3 stacking faults per crystallite, an aspect ratio of ~ 1.3 along the (002) direction, and a relaxed surface. These particles are small enough that surface contributions cannot be completely ignored. All three deviations from ideality are required to properly fit the full spectrum. Each deviation affects the spectrum independently and in different regions. The stacking faults mostly affect the area between $2\theta \sim 30^\circ$ and 50° , the prolate shape affects the peak position of the first diffraction feature at $2\theta \sim 25^\circ$, and the surface disorder affects the shape of the first feature.

(26) (a) Duke, C. B.; Patterson, A.; Wang, Y. R.; Stiles, K.; Kahn, A. *Surf. Sci.* 1988, 197, 11. (b) Wang, Y. R.; Duke, C. B. *Phys. Rev. B* 1988, 37, 6417. (c) Horvay, T. N.; Brandes, G. R.; Carter, K. F.; Duke, C. B.; Patterson, A.; Lester, D. L.; Kahn, A.; Horng, S. F.; Stevens, K.; Stiles, K.; Mills, A. P. *J. Phys. Rev. B* 1992, 46, 7011.

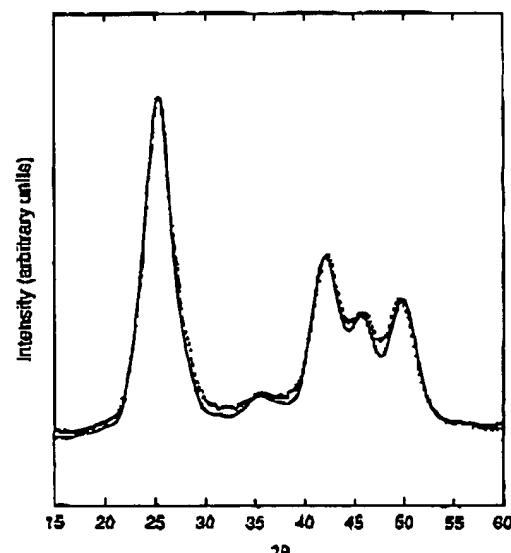


Figure 15. Experimental X-ray powder diffraction spectrum of $\sim 37\text{ \AA}$ (~ 1000 atoms) diameter crystallites (dotted line) compared with a simulated spectrum (solid line) for wurtzite crystallites containing ~ 1000 atoms with one stacking fault per crystallite in the (002) direction, an aspect ratio of 1.3 along the (002) axis, and a small amount of surface disorder.

In summary, powder X-ray diffraction patterns of a series of CdSe samples can be fit with computer simulations using parameters consistent with TEM and EXAFS investigations. These simulations assume a bulk crystal structure and rely on a small number of parameters (seven) to develop a working description of average crystallite morphology. These parameters are the lattice constant, the amount of thermal disorder (Debye-Waller factor), crystallite size, aspect ratio, stacking fault defect density, the amount of surface disorder, and a constant background correction. As noted above, each parameter affects the powder pattern independently and in a different region, giving a robust fit. Of these seven parameters, two are fixed from TEM and EXAFS data: The lattice constant is fixed at the bulk value (EXAFS) and the crystallite size if taken from TEM measurements. Of the remaining five parameters, four (aspect ratio, surface disorder, background correction, Debye-Waller factor) are fit for one crystallite size and then fixed at that value for the whole series of sizes. As noted, these four parameters are also consistent with independent structural probes. The remaining parameter, the average stacking fault defect density, is allowed to float from size to size. Its value is however relatively constant over the entire series of sizes.

The combination of X-ray studies and TEM imaging yields a description of average CdSe nanocrystallite structure. Strict classification of the structure as purely wurtzite or zincblende is potentially misleading. TEM images of crystallites grown slowly at high temperature provide dimensions of slightly prolate particles and indicate the presence of stacking faults in the (002) direction. Diffraction patterns are consistent with a predominantly wurtzite structure averaging one stacking fault defect every 6–7 planes in the elongated (002) direction. The presence of planar disorder may be important in understanding the influence of structure on the electronic properties and phase stabilities of nanocrystallites. The prolate shape results in a greater coherence length in the (002) direction and provides a potential explanation for the apparent shift in the first diffraction peak without requiring significant lattice contractions or phase transitions. A small amount of surface disorder, consistent with TEM and EXAFS observations, improves agreement between simulated and experimental diffraction spectra but does not uniquely define a surface structure.

*Synthesis of CdE Semiconductor Nanocrystallites***IV. Conclusion**

A relatively simple route to the synthesis of macroscopic quantities of nearly monodisperse II-VI semiconductor nanocrystallites is presented. The technique allows an entire series of samples, ranging from ~ 12 to 115 \AA in diameter, to be obtained in a single reaction and in macroscopic quantities. The particles produced have uniform size, shape, and surface passivation and show relatively sharp absorption and emission features at room temperature.

The combination of TEM imaging and comparisons of experimental and simulated X-ray diffraction spectra provides a self-consistent description of crystallite structure. These studies highlight the importance of shape and disorder in interpreting experimental results. Average bulk bond lengths and a predominantly hexagonal (wurtzite) crystal structure are found, even in crystallites containing as few as 275 atoms ($\sim 20\text{ \AA}$ diameter).

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The synthetic rationale and systematic structural analysis presented here should be generalizable to the production of a variety of new nanocrystalline materials.

Acknowledgment. We thank Mike Frangillo and Bashir Dabbousi for valuable assistance with the transmission electron microscopy, Peter Nelson for helping set up the computer modeling, and Vicki Colvin for useful discussions. C.B.M. and D.J.N. gratefully acknowledge fellowships from NSERC and NSF, respectively. This research was funded in part by the MIT Center for Materials Science and Engineering (NSF-DMR-90-22933), NSF (DMR-91-57491, CHE-89-14953, and ECS-91-18907), the donors of the Petroleum Research Fund, administered by the American Chemical Society (ACS-PRF-24398-G6), and the Lucille and David Packard Foundation.

Colloidal synthesis of nanocrystals and nanocrystal superlattices

by C. B. Murray
Shouheng Sun
W. Gaschler
H. Doyle
T. A. Betley
C. R. Kagan

This paper provides an overview of the synthetic techniques used to prepare colloidal nanocrystals (NCs) of controlled composition, size, shape, and internal structure and the methods for manipulation of these materials into ordered NC assemblies (superlattices). High-temperature solution-phase synthesis (100–300°C) is followed by size-selective separation techniques in the preparation of monodisperse NC samples tunable in size from ~1 to 15 nm in diameter with <5% standard deviation. Each NC consists of a crystalline inorganic core coordinated by an organic monolayer. These monodisperse NC samples enable systematic studies of structural, electronic, magnetic, and optical properties of materials as a function of size evolution from molecular species (<100 atoms) to bulk solids (>100 000 atoms). We illustrate size-dependent properties for magnetic materials using Co and for semiconducting materials using PbSe. These NC samples are sufficiently uniform in size to self-assemble into close-packed, ordered NC superlattices, also known as colloidal crystals.

Introduction

Cooperative interactions between atoms in condensed matter produce the physical properties that are recognized as characteristic of bulk solids. The natural length scale of many of these physical phenomena lies between 1 and 15 nm (10^2 and 10^5 atoms). In nanometer-scale structures, finite size effects give rise to novel electronic, magnetic, optical, and structural properties. The desire to identify, understand, and exploit the size-dependent properties of materials at the nanometer scale motivates the study of monodisperse nanometer-scale crystals, known as nanocrystals (NCs). For example, magnetic [1–5] and semiconductor [6–9] NCs exhibit strong size-dependent properties that may provide insight into the scaling limits of magnetic storage and microelectronics, key components in information technology.

Preparation of NC samples that are uniform in composition, size, shape, internal structure, and surface chemistry is essential to successfully mapping their size-dependent materials properties. High-temperature solution-phase synthesis provides a method of preparing such uniform NC samples for a variety of metals [5, 10] and semiconductors [9, 11]. Each NC in a sample consists of an inorganic crystalline core surrounded by an organic monolayer. Structural and chemical probes of the

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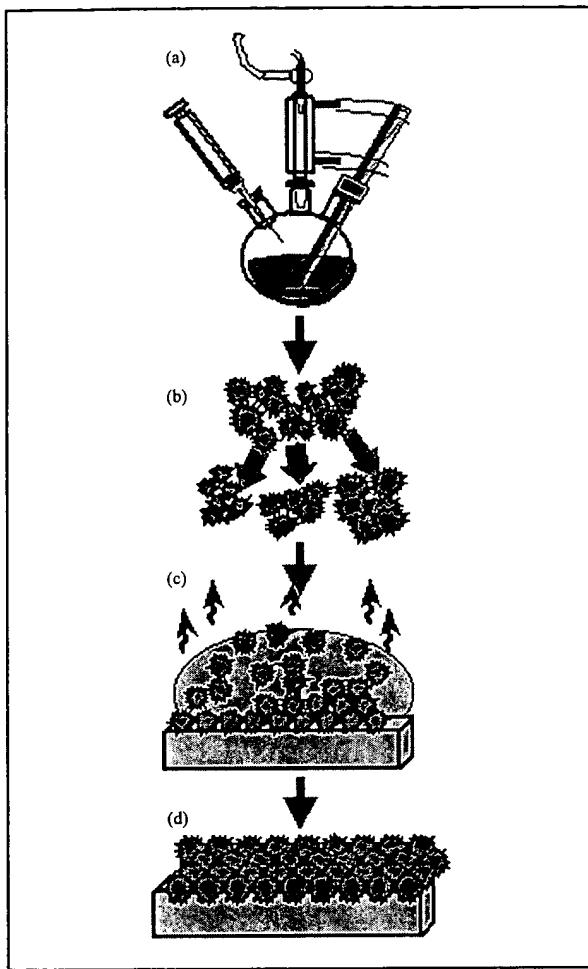


Figure 1

Schematic representation of the synthetic procedures to (a) synthesize NC samples by high-temperature solution-phase routes, (b) narrow the NC sample size distribution by size-selective precipitation, (c) deposit NC dispersions that self-assemble, and (d) form ordered NC assemblies (superlattices).

inorganic core and the organic monolayer are necessary to develop structural models of NC samples. Only with careful characterization can the size-dependent magnetic, optical, and electronic properties characteristic of the NCs in the sample be uncovered.

These NC samples may then be used as the building blocks for close-packed NC solids. The organic monolayer coordinating each NC surface enables uniform NC samples, under controlled conditions, to self-assemble into NC superlattices [5, 12]. These hybrid organic-inorganic materials combine the unique properties characteristic of the "individual" NC with new collective properties arising from interactions between neighboring NCs in the

superlattice [13, 14]. Controlling the size and composition of the NCs and the length and chemical functionality of the organic monolayer allows the properties of the individual NC building blocks and the collective properties of the NC superlattices to be engineered.

General synthesis of monodisperse inorganic NCs and NC superlattices

A general scheme for preparing monodisperse NC samples (with <5% standard deviation in size) requires a single, temporally short nucleation event followed by slower growth on the existing nuclei. This may be achieved by rapid addition of reagents into a reaction vessel containing a hot, coordinating solvent [Figure 1(a)] [11]. The temperature of the solution is sufficient to decompose the reagents, forming a supersaturation of species in solution that is relieved by nucleation of NCs. Upon nucleation the concentration of these species in solution drops below the critical concentration for nucleation, and further material can only add to the existing nuclei.

An alternative synthetic approach involves mixing the reagents in a vessel at a temperature low enough to preclude any appreciable reaction. A controlled ramp of the solution temperature accelerates the chemical reaction and produces the requisite supersaturation, which is then relieved by a burst of nucleation. As long as the temperature is adjusted to keep the rate at which the reagents react less than or equal to the rate at which material adds to the existing nuclei, the supersaturated state is never revisited and no new nuclei form. In either approach, the size distribution of the NC sample is limited primarily by the short time interval in which the nuclei form and begin to grow.

The systematic adjustment of the reaction conditions—time, temperature, and concentration and chemistry of reagents and surfactants—can be used to control NC size and thus prepare a size series of NC samples. In general, NC size increases with increasing reaction time, as more material adds to NC surfaces, and with increasing temperature, as the rate of addition of material to the existing nuclei increases. Many systems also exhibit a second, distinct, growth stage known as Ostwald ripening, in which the high surface energy of the smaller NCs promotes their dissolution, while material is redeposited on the larger NCs. The average NC size increases over time, with a compensating decrease in NC number. Higher solution temperatures enhance Ostwald ripening, also leading to larger average NC size.

Tailoring the ratio of the concentration of reagents to that of surfactants provides another control over NC size, since high stabilizer-to-reagent concentrations favor the formation of more small nuclei initially and thus a smaller NC size [10]. The chemistry of the surface agent can also be chosen to control NC size. During NC growth, the

surfactants in solution adsorb reversibly to the surfaces of the NCs, providing a dynamic organic shell (capping layer) that stabilizes the NCs in solution and mediates their growth. Surfactants that bind more tightly to the NC surface or larger molecules providing greater steric hindrance (bulkier surfactants) slow the rate of materials addition to the NC, resulting in smaller average NC size. For example, bulkier trioctylphosphines provide larger steric hindrance than more compact tributylphosphines, slowing NC growth. An effective strategy involves using a pair of surface agents of which one binds tightly to the NC surface, hindering growth, and the other is less tightly bound, permitting rapid growth. For example, judicious adjustment of the ratio of carboxylic acid (tightly bound) and alkylphosphine (weakly bound) stabilizers allows the growth rate and therefore the size of the NCs to be controlled (see discussion of Co NCs below).

Alternatively, the size of NC samples may also be increased by supplying additional reagent feedstock to a solution of growing NCs. As long as the rate of feedstock addition does not exceed the rate of material addition to the NCs, the NCs continue to grow without creation of new nuclei. This controlled addition of reagents can be optimized to narrow or “focus” the NC size distribution as material adds to all NCs at nearly equal rates and produces an initial variation in NC size that is small compared to the larger, final size of the NCs [15].

When the NC sample reaches the desired size, further growth is arrested by cooling the solution. The NC dispersions are stable if the interaction between the capping groups and the solvent is favorable, providing an energetic barrier to counteract the van der Waals and magnetic (for magnetic materials) attractions between NCs. The NCs are then isolated from their growth solution. Introducing a nonsolvent that is miscible with the first solvent but has an unfavorable interaction with the capping groups (hence “nonsolvent”) reduces the barrier to aggregation and destabilizes the NC dispersion, causing their flocculation. Centrifuging the resulting turbid suspension allows the solvent to be decanted and powders of the NCs to be isolated. These powders consist of the desired NCs and their intimate organic capping layer and can be redispersed in a variety of solvents.

The general synthetic approaches described in this paper can be optimized to yield size distributions $\sigma \leq 10\%$ in diameter, which can then be further narrowed to $\sigma \leq 5\%$ through size-selective precipitation, as depicted in Figure 1(b). Size-selective precipitation involves the slow titration of a nonsolvent into the dispersion to bring about its partial flocculation [11, 16]. Since the largest NCs experience the greatest attractive forces, they aggregate first. If the dispersion is allowed to flocculate only partially, filtering or centrifuging the suspension isolates a precipitate enriched in the larger NCs and leaves the

smaller NCs dispersed in the supernatant, which is then decanted. Additional nonsolvent may be added to the supernatant to isolate a second fraction of smaller NCs. The precipitates isolated can in turn be redispersed in a solvent and subjected recursively to this gentle destabilization/redispersion procedure to further narrow the sample size distribution. Narrower initial size distributions allow the desired σ value to be attained with fewer stages of size-selective precipitation and thus provide higher yields.

The monolayer of organic capping groups bound to the NC surface can be exchanged with other competing capping groups. Repeated exposure of the NCs to an excess of the competing capping groups, followed by precipitation and redispersion in fresh solvent, isolates cap-exchanged NCs [9]. This process allows the length and chemical functionality of the organic capping layer to be precisely adjusted.

NC samples with narrow size distributions can be deposited from solvents to assemble into NC superlattices (also known as colloidal crystals), as depicted in Figures 1(c) and 1(d). The solvent used to deposit the NC superlattices is selected for its polarity and for its boiling point. The solvent polarity is chosen so that the interaction between NCs will become mildly attractive as the solvent evaporates and the dispersion becomes more concentrated. The boiling point of the solvent is selected to permit the NCs enough time to find equilibrium lattice sites before the solvent evaporates on the growing NC superlattice.

The NC superlattices formed are waxy solids held together by weak van der Waals and dipolar magnetic attractions. They may be made more rigid and robust by selecting organic capping groups that will cross-link upon exposure to radiation (UV or electron beam) or upon heating. For example, heating an NC superlattice to $\sim 300^\circ\text{C}$ under one atmosphere of an inert gas, such as argon, cross-links some organic capping groups, forming an amorphous carbon matrix between NCs in the superlattice [5, 17]. In many NC superlattice systems, heating under vacuum leads to desorption of the organic capping groups and controlled sintering of the NCs into a fully inorganic solid [9].

Nanocrystal magnets: Monodisperse cobalt NCs

The synthesis of metal colloids has been studied for more than a century, and yet the number of preparations yielding a size series of monodisperse transition metal NC samples remains relatively small [18]. Cobalt serves as a model system for magnetic scaling in materials because its low to moderate crystal anisotropy allows the effects of size, shape, internal crystal structure, and surface anisotropy to be observed in a single system. Synthetic

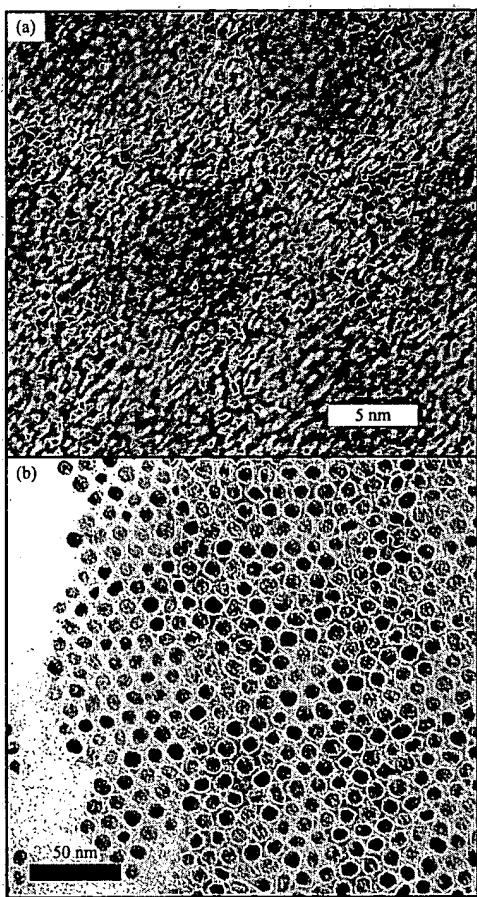


Figure 2

(a) High-resolution TEM image of 7-nm hcp Co NCs revealing subtle lattice imaging of the NCs. (b) Lower-resolution TEM images of an ensemble of 10-nm hcp Co NCs.

methods allow Co NCs to be produced in several distinct crystal polymorphs with varying degrees of crystal perfection. Here we focus on two synthetic procedures that are used to prepare Co NCs with crystal structures closely related to the bulk hexagonal close-packed (hcp) and face-centered cubic (fcc) structures. A third chemical route produces Co NCs with a metastable cubic internal crystal structure, recently labeled ε -Co; it has been reported in detail elsewhere [10, 19].

hcp Co NCs

High-temperature (100–300°C) reduction of metal salts in the presence of stabilizing agents has been employed to produce monodisperse Co NCs 2–12 nm in diameter. Standard air-free techniques are used. For example, in a

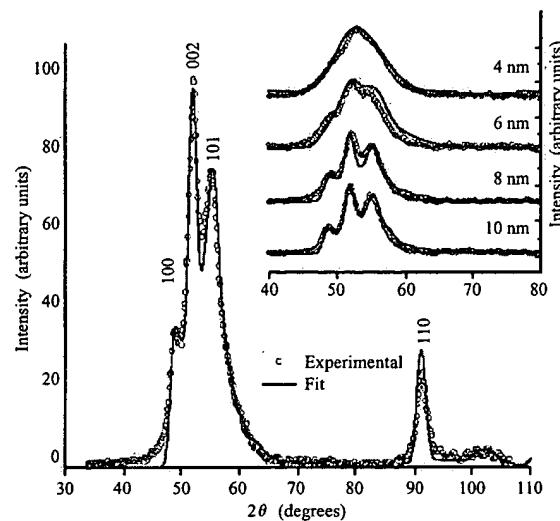


Figure 3

Wide-angle X-ray diffraction pattern of 10-nm hcp Co NCs (open circles) and computer simulation (solid curve) generated by including the statistics of size, internal structure, and shape from TEM measurements. Inset shows the WAXS patterns for a size series of hcp Co NCs, highlighting the effects of finite size broadening on the X-ray reflections.

typical reaction used to prepare 6–8-nm Co NCs, 1.0 g (4 mmol) $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ is combined with 1.28 mL (4 mmol) oleic acid in a flask containing 40 mL diphenylether. The solution is heated to 200°C under a N_2 purge. As the solution is heated, H_2O is distilled out, and the purple color of the cobalt acetate tetrahydrate changes to a deep “cobalt blue.” When the reaction mixture reaches 200°C, ~2.0 mmol trioctylphosphine is added to the solution. The bulky trioctylphosphine stabilizer provides a greater steric hindrance to the addition of cobalt species than the more compact tributylphosphine, slowing the Co NC growth rate. Tributylphosphine is substituted for trioctylphosphine in the preparation of larger NCs. The reaction mixture is then heated to 240°C.

In a separate flask, 2.1 g of a mild reducing agent, 1,2 dodecanediol (1,2 hexadecanediol may also be used) is dissolved in 10 mL of octylether and heated to 80°C. This solution is transferred using a syringe with a wide-bore needle (~12 gauge) and delivered through a septum into the hot (240°C) reaction vessel. The color of the solution changes from blue to black over a period of two minutes as the Co NCs nucleate and grow. The solution is held at 240°C for ~10 minutes until all of the reagents are consumed. The dispersion is cooled, and ethanol is added to isolate Co NCs as an air-stable black magnetic precipitate. This preparation yields Co NC samples with a

size distribution $\sigma \sim 10\%$, which is then further narrowed by size-selective precipitation to $\sigma \sim 5\%$.

Although no Ostwald ripening is observed in this preparation, NC size is coarsely tunable by adjusting the ratio of the concentration of capping groups to that of the metal salt and by selecting the degree of bulkiness of the organophosphine stabilizer. Higher metal-to-stabilizer ratios result in larger Co NCs, while more bulky organophosphines (e.g., trioctylphosphine) favor smaller NCs.

Figure 2(a) shows a high-resolution transmission electron microscope (HRTEM) image of several $\sim 7\text{-nm}$ Co NCs. Careful inspection reveals lattice spacing of $\sim 2\text{ \AA}$, consistent with the 2.02-\AA lattice spacing for the (002) planes and the 1.91-\AA spacing for the (101) planes of hcp Co. Surveys of a number of such HRTEM images and electron diffraction studies indicate that the NCs are predominantly hcp but show evidence of stacking faults along the (002) axis. Lower-magnification TEM is used to image large numbers of NCs and to compile the statistics of NC size, size distribution, and shape for NC samples. A representative TEM image of $\sim 10\text{-nm}$ Co NCs with a sample size distribution $\sigma \sim 6\%$ is shown in **Figure 2(b)**. Within this TEM image, the appearance of some “darker” NCs results from enhanced diffraction contrast due to their orientation with respect to the electron beam. While there are contrast variations between the individual NCs in the sample, each NC has near-uniform contrast consistent with each NC having a single-crystal orientation and thus a single-crystalline core.

The statistical descriptions of NC sample size, shape, internal structure, and size distribution extracted from TEM images and electron diffraction patterns are used to generate an atomistic model of the NC ensemble. This model in turn is used to calculate the expected wide-angle X-ray scattering (WAXS) patterns for NC samples and can be compared with experimental diffraction patterns. The model is then refined to provide the best simultaneous fit to the TEM results and the powder X-ray diffraction measurements [9, 11]. WAXS patterns collected for hcp Co NC samples (open circles) and the corresponding computer simulations (solid curves) are shown in **Figure 3**. These Co NC samples are consistent with a largely hcp internal structure with fcc stacking faults along the (002) direction. The inset shows the size evolution of the X-ray diffraction patterns for hcp Co NC samples ranging in size from 4 to 10 nm in diameter. The X-ray reflections are broadened in smaller NC samples by finite size effects, and in all samples the (100), (102), and (103) reflections are further broadened and attenuated by the stacking faults along the c-axis.

Each Co NC is a single-domain magnet. Below a critical temperature (known as the blocking temperature), the magnetic moment of the NC is pinned along an “easy”

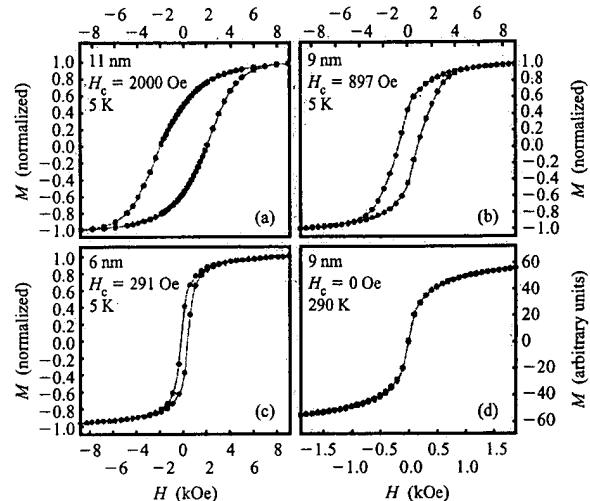


Figure 4

Magnetization versus field (M vs. H) hysteresis loops at 5 K for (a) 11-nm, (b) 9-nm, and (c) 6-nm hcp Co NC samples. Comparison of M vs. H loops for 9-nm hcp Co NCs at (b) 5 K and (d) 290 K.

axis and is said to be ferromagnetic. Above the blocking temperature, thermal fluctuations are sufficient to cause the magnetic moment to rotate between the various easy axes in the NC. This fluxional state leads to a randomization of the magnetic moments, and no hysteresis is observed.

The energetic barrier pinning the NC magnetic moment and preventing its relaxation is proportional to the product of the anisotropy constant (K) and the volume of the NC (V). The anisotropy constant includes contributions from magnetocrystalline shape and surface anisotropies. After the saturating magnetic field is removed, the magnetization, M , of an ensemble of noninteracting, single-domain NCs decays in time as $M(t) \propto e^{-t/\tau}$, where τ is exponentially proportional to KV . The double exponential dependence of $M(t)$ on KV highlights the necessity to prepare NC samples with narrow size distributions and well-controlled crystal anisotropies to avoid significant broadening of the ferromagnetic to superparamagnetic transition.

Figures 4(a), 4(b), and 4(c) respectively show the size-dependent M vs. H hysteresis loops at 5 K for hcp Co NCs of 11-nm, 9-nm, and 6-nm diameter. As the size of the NC decreases, the width of the hysteresis loop decreases as the energetic barrier KV decreases. Comparison of hysteresis loops for 9-nm hcp Co at 5 K [**Figure 4(b)**] and 290 K [**Figure 4(d)**] shows the randomization of the magnetic moments, transforming the material from ferromagnetic to superparamagnetic due to the influence of temperature.

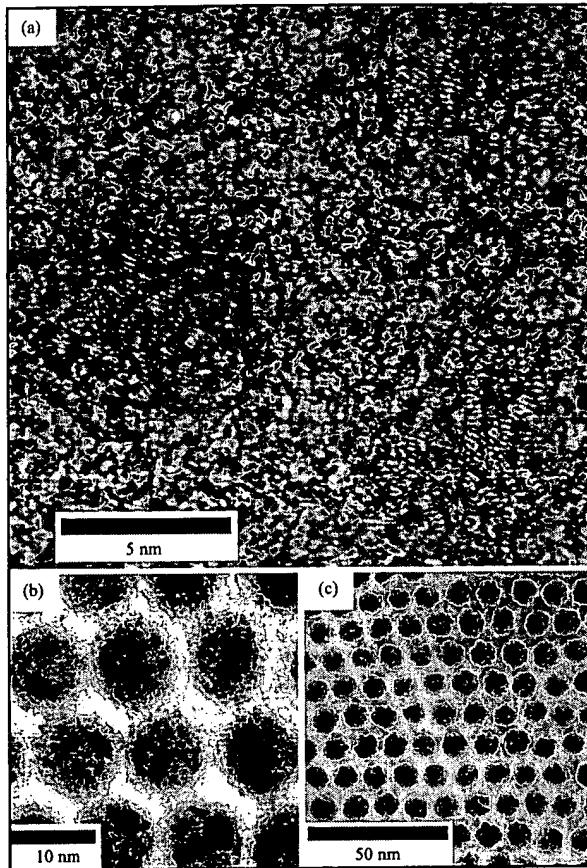


Figure 5

(a) High-resolution TEM image for several 7-nm multiply twinned fcc (mt-fcc) Co NCs. (b), (c) Low-resolution TEM images of ensembles of 9-nm mt-fcc Co NCs. Note the contrast variations within an individual NC in the image (see description in text).

Multiply twinned FCC Co NCs

A second polymorph of Co NCs, in which each NC comprises multiple fragments of the bulk fcc lattice, may be prepared by thermal decomposition of cobalt octacarbonyl $[Co_2(CO)_8]$ in the presence of stabilizing ligands. Variations on this procedure have been known for years to produce metal NCs when oxygen is excluded from the reaction [20], and to prepare metal oxide NCs when oxygen/air is introduced during the reaction [21, 22]. We report a refined synthesis using $Co_2(CO)_8$ as a precursor to prepare multiply twinned fcc (mt-fcc) Co NC samples with narrow size distributions. Standard air-free handling procedures are again employed until the NC growth is complete. In a typical synthesis for ~8- to 10-nm mt-fcc Co, a reaction vessel containing 30 mL diphenylether (one could use octylether, but it is significantly more costly), 2 mmol (0.64 mL) oleic acid, and 2.0 mmol

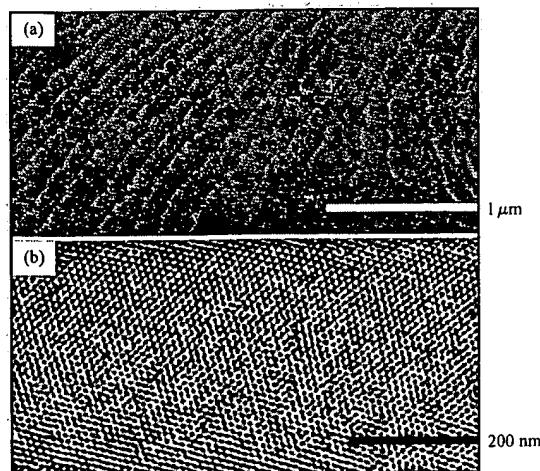


Figure 6

(a) High-resolution scanning electron micrograph of a 10-nm Co NC superlattice. (b) Low-resolution TEM image of an 8-nm Co NC superlattice.

tributylphosphine is heated under a N_2 flush to 200°C. In a separate flask, 684 mg $Co_2(CO)_8$ is combined with 10 mL dioctylether, warmed to 60°C under a flush of N_2 , and stirred until fully dissolved. The $Co_2(CO)_8$ solution in dioctylether is viscous and is therefore transferred in a syringe with a wide-bore needle (~12 gauge). The solution is rapidly injected through a septum into the hot vessel (200°C) containing the diphenylether solvent and the oleic acid and organophosphine stabilizers. Upon injection, the solution turns black in color and bubbles as $Co_2(CO)_8$ decomposes, nucleating Co NCs and releasing CO gas. This solution is then heated at 200°C for ~15 minutes and vigorously stirred. The NC dispersion is cooled to room temperature, and the NCs are isolated from solution as described above for hcp Co NC samples.

Figure 5 shows high- and low-resolution TEM images of the mt-fcc NC samples. HRTEM images, as shown in Figure 5(a) for several ~7-nm NCs, reveal complicated interference patterns at a resolution sufficient to image the lattice. The patterns are consistent with multiple crystal orientations contained within a single NC [23]. This is also seen in lower-resolution TEM images, as shown in Figures 5(b) and 5(c). The contrast variations within each NC arise because lattice fragments are at different orientations with respect to the electron beam.

More detailed magnetic studies of these multiply twinned NCs will allow comparison with size-dependent trends in better-crystallized hcp and ϵ -Co NC samples. These studies will highlight the importance of internal

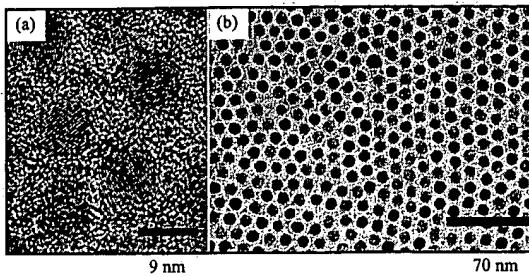


Figure 7

TEM micrographs of PbSe (a) at high resolution, revealing lattice imaging of the NCs; (b) at low resolution, showing an ensemble of NCs.

crystal structure on the magnetic properties of nanocrystalline material.

The narrow size distribution of NC samples prepared by this synthetic route allows these NCs to self-assemble from solution into ordered arrays. For example, superlattices of oleic-acid-capped Co NCs are deposited by dispersing the NC sample in either hexane or a mixture of hexane and octane, depositing the NC dispersion on a substrate surface, and covering the solution/substrate with a petri dish to slow the rate of solvent evaporation. Slowing the rate of solvent evaporation allows sufficient time for NCs from solution and on the surface to find equilibrium lattice sites on the growing NC superlattice. Figure 6(a) shows a high-resolution scanning electron microscope (HRSEM) image of a NC superlattice composed of 10-nm mt-fcc Co NCs. Well-ordered terraces, ledges, and kinks are apparent as NCs add to the growing superlattice, much like atoms on a growing crystal surface. Low-resolution TEM imaging [Figure 6(b)] shows a projection of a superlattice formed from 8-nm Co NCs.

Nanocrystal semiconductors—PbSe NCs (quantum dots)

PbSe NCs are synthesized by rapidly injecting a room-temperature solution of lead oleate and trioctylphosphine selenide dissolved in trioctylphosphine into a rapidly stirred solution containing diphenylether at 150°C.¹ Upon injection, small (<2-nm) PbSe NCs nucleate and begin to grow, even as the solution temperature drops toward 80°C because of the addition of the room-temperature reagents. Raising the solution temperature accelerates the NC growth rate, and higher temperatures are used to prepare large-size NCs. Solution temperatures of 90 to 220°C are used to tune the size of PbSe NC samples from 3.5 nm to

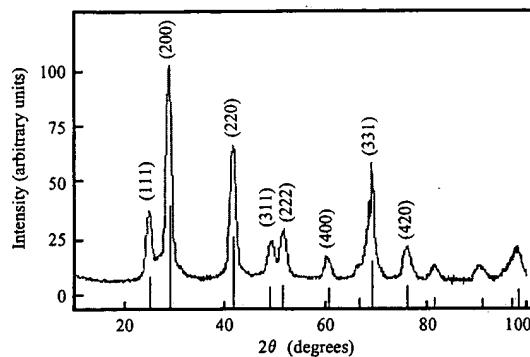


Figure 8

Wide-angle X-ray diffraction pattern of 10-nm PbSe NCs indexed to the bulk rock-salt crystal structure.

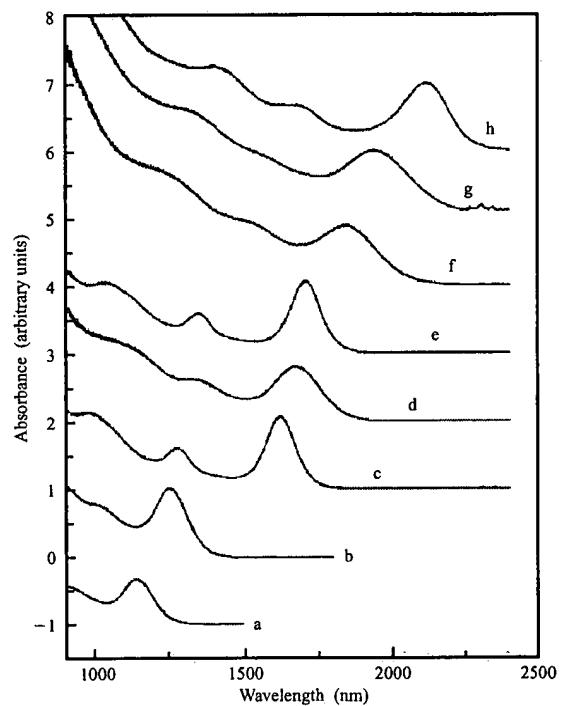


Figure 9

Room-temperature optical absorption spectra for a series of PbSe NC samples measuring (a) 3.0 nm, (b) 3.5 nm, (c) 4.5 nm, (d) 5 nm, (e) 5.5 nm, (f) 7 nm, (g) 8 nm, and (h) 9 nm in diameter.

15 nm in diameter. PbSe NC samples can be isolated from solution within ~15 minutes of the precursor injection.

¹ W. Gaschler and C. B. Murray, "Synthesis of Lead Selenide Nanocrystals: Quantum Cubes and Quantum Spheres," work in preparation.

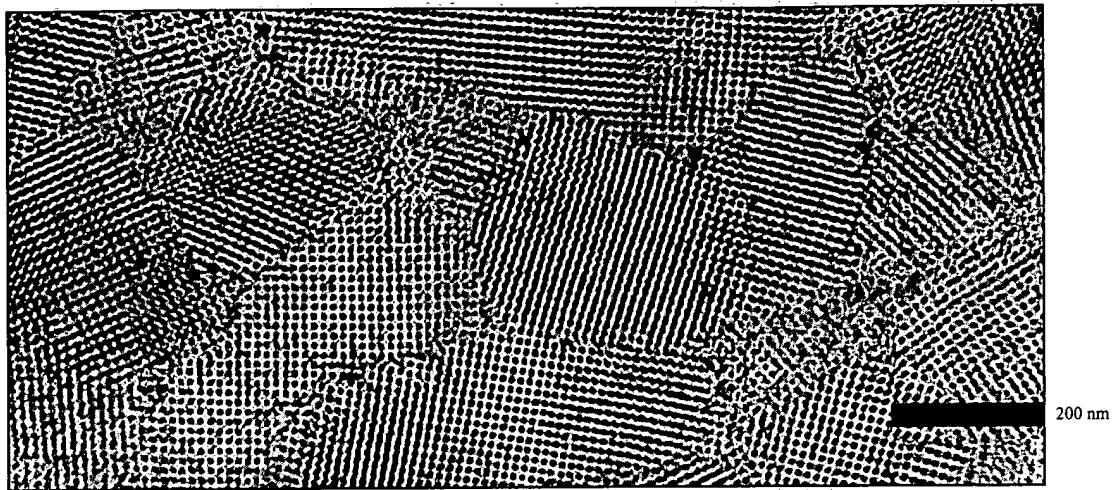


Figure 10

TEM micrograph of a superlattice of 8-nm PbSe NCs.

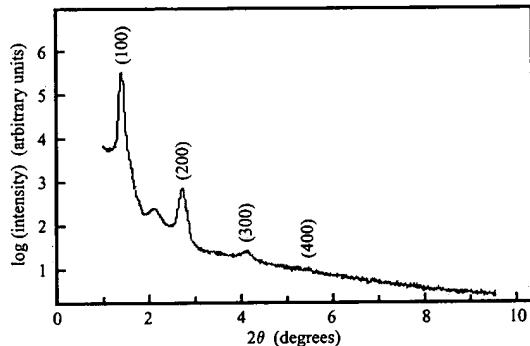


Figure 11

Small-angle X-ray scattering of an 8-nm PbSe NC superlattice indexed to a simple cubic structure.

After the PbSe NCs reach the desired size, the dispersion is cooled and short-chain alcohols are added to flocculate the NCs, which are then separated from solution by centrifuging. The NC size distribution $\sigma \sim 10\%$ is further narrowed by size-selective precipitation to 5% or better. Figure 7(a) shows a high-resolution TEM image of ~ 8 -nm PbSe NCs. The internal crystal lattice is clearly resolved in several NCs. Lower-magnification imaging [Figure 7(b)] shows the consistent size and shape of the PbSe NCs within a sample. As the surface coverage

of NCs approaches one monolayer, these uniform NC samples begin to be ordered into close-packed assemblies. WAXS patterns for 10-nm PbSe NCs [Figure 8] match the bulk rock-salt structure (bulk reflections indicated as lines from the 2θ axis). TEM images and X-ray diffraction patterns show that the individual PbSe NCs are single crystals of the bulk rock-salt lattice and show no signs of faulting.

Semiconductor NCs smaller in size than the bulk exciton Bohr radius confine electronic excitations in all three dimensions. Three-dimensional confinement effects collapse the continuous density of states of the bulk solid into the discrete electronic states of the NC. For PbSe, the bulk Bohr radius is 46 nm. In Figure 9, optical absorption spectra for a size series of PbSe NC samples, ranging in size from 3.0 nm to 9 nm in diameter, show the expected size-dependent effects of quantum confinement. As the NC diameter decreases, the absorption edge shifts to the blue, and the separation between electronic transitions increases.

Figure 10 shows a TEM image of a three-dimensional superlattice of oleic-acid-capped 8-nm PbSe NCs. The PbSe NCs pack in a simple cubic lattice with the long organic ligands filling the interstices between NCs in the superlattice. In this image a number of ordered domains have nucleated simultaneously and have grown together, providing a mosaic texture to the thin film. Small-angle X-ray scattering (SAXS) measurements, as shown in Figure 11, reveal reflections arising from the scattering of X-rays off the planes of the NC superlattice [9, 12].

Indexing of the reflections in the SAXS pattern is consistent with the simple cubic NC superlattice imaged in TEM and shows that the NC superlattice is preferentially (100)-oriented with respect to the substrate surface.

Conclusion

High-temperature solution-phase syntheses yield magnetic and semiconductor NC samples that are uniform in size to \pm one atomic layer, composition, shape, internal structure, and surface chemistry. Systematic study of a series of NC sizes permits the size-dependent electronic, magnetic, and optical properties of nanometer-size materials to be mapped. Under controlled deposition conditions, NC samples that are sufficiently uniform in size self-assemble from solutions to form ordered NC arrays. The size and composition of the NCs and the length and chemical functionality of the organic capping layer can be tailored to engineer the physical properties of NC superlattices.

Acknowledgments

Dr. Gaschler's research was supported by the Defense Advanced Research Projects Agency through ARO Grant No. DAAD19-99-1-0001.

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Received December 5, 2000; accepted for publication January 5, 2001

Christopher B. Murray *IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 (cbmurray@us.ibm.com)*. Dr. Murray is the manager of the Nanoscale Materials and Devices Department and contributes to the preparation and characterization of nanoscale materials. He joined IBM in 1995 after completing his Ph.D. studies in chemistry at MIT.

Shouheng Sun *IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 (ssun@us.ibm.com)*. Dr. Sun is a materials chemist who has developed leading synthetic routes for the preparation of monodisperse magnetic nanostructures. He joined IBM in 1996 after completing his Ph.D. studies in chemistry at Brown University.

Wolfgang Gaschler *BASF AG, Akiengesellschaft, ZKD-B001, Germany (Wolfgang.Gaschler@basf-ag.de)*. Dr. Gaschler was a visiting scientist at the IBM Thomas J. Watson Research Center from 1999 to 2000. He carried out studies on semiconductor nanocrystal superlattices in collaboration with the Advanced Materials Research Institute (AMRI) at the University of New Orleans, Louisiana.

Hugh Doyle *National Microelectronics Research Center, University College Cork, Lee Maltings, Cork, Ireland (hugh_doyle@hotmail.com)*. Dr. Doyle was a visiting scientist at the IBM Thomas J. Watson Research Center from 1998 to 2000 developing computational models of nanoscale structures. He joined IBM in 1998 after completing his Ph.D. studies in chemistry at the University College of Dublin, Ireland.

Theodore A. Betley *California Institute of Technology, Division of Chemistry and Chemical Engineering, 1200 E. California Blvd., Pasadena, California 91125 (betley@its.caltech.edu)*. In 1999 Mr. Betley worked as a summer intern at the IBM Thomas J. Watson Research Center in Yorktown Heights, New York, contributing to the synthesis of monodisperse magnetic nanocrystals. In 2000, upon completing his bachelor's degree in chemical engineering at the University of Michigan, Mr. Betley began his graduate studies in chemistry at the California Institute of Technology.

Cherie R. Kagan *IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 (cheriek@us.ibm.com)*. Dr. Kagan is a Research Staff Member in the Physical Sciences Department at the IBM Thomas J. Watson Research Center. She received a B.S.E. degree in materials science and engineering and a B.A. degree in mathematics, both from the University of Pennsylvania, in 1991. In 1996, she received her Ph.D. degree in electronic materials from MIT. Her thesis work focused on the self-assembly of close-packed solids of semiconductor nanocrystals and the unique electronic and optical properties that arise from cooperative interactions between neighboring nanocrystals. In 1996, Dr. Kagan went as a Postdoctoral Fellow to Bell Laboratories, where she built a scanning confocal Raman microscope to study the formation of holograms in multicomponent photopolymers. In 1998 she joined IBM, where she has been investigating the optical and electrical properties of organic-inorganic hybrid materials and the application and patterning of organic-inorganic hybrids and soluble organic semiconductors in thin-film field-effect transistors.